

Spatial Characterization of PM_{2.5} Associated Organic Compounds

CRPAQS Annual Average Data Presentation

Lynn R. Rinehart and Barbara Zielinska

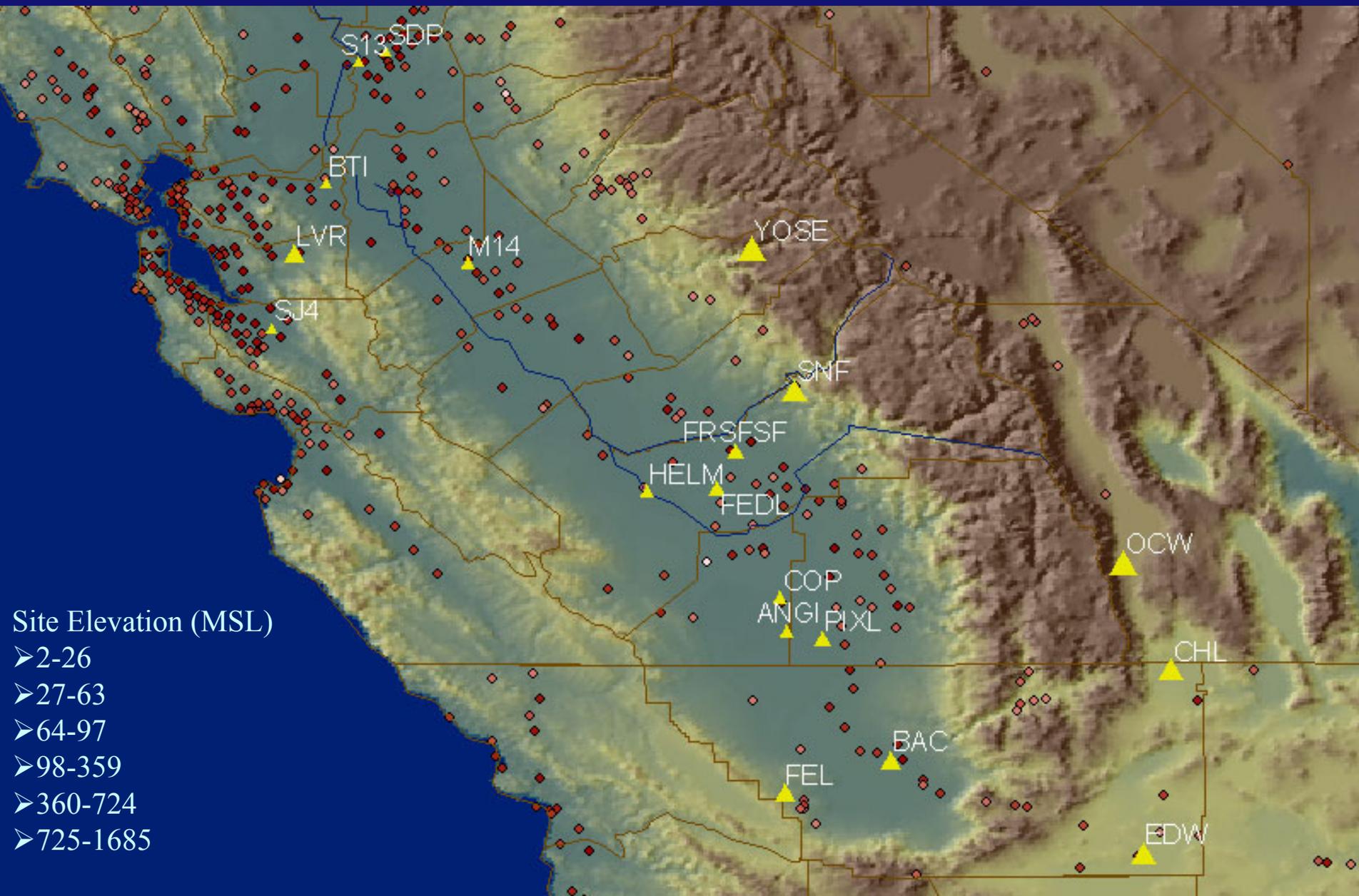
March 9th, 2004



Annual Average Sites Background

ID	Site Name	Purpose
ANGI	Angiola	intrabasin gradient; vertical gradient; visibility
BAC	Bakersfield California Avenue	community exposure; visibility
BTI	Bethel Island	interbasin transport
CHL	China Lake	visibility
COP	Corcoran	community exposure
EDW	Edwards	intrabasin gradient; visibility
FEDL	Dairy (near Raisin City)	source-animals
FEL	Fellows	source-oil fields
FRS	Fresno Residential	source-woodburning
FSF	Fresno First St	community exposure; visibility
HELM	Helm	intrabasin gradient
LVR	Livermore	interbasin transport
M14	Modesto	community exposure
OCW	Olancha	background; visibility
PIXL	Pixely Wildlife Refuge	intrabasin gradient
S13	Sacramento T Street	community exposure
SDP	Sacramento Del Paso	community exposure
SJ4	San Jose 4th Street	community exposure
SNF	Sierra Nevada Foothills	vertical gradient; intrabasin gradient; visibility
YOSE	Yosemite	background; visibility

Elevation of AA Satellite Sites



Sample Extraction & Preparation

- Complete Set of Mini-Vol Filters Combined
- Deuterated Internal Standards
- Solvent Extraction by DCM & Acetone
- Concentration & Filtration
- Extract Split into 2 Equivalent Fractions
 - Non-polar analysis
 - Polar analysis

Compound List: PAH and Polar Organics

Naphthalene	Anthrone	hexanoic acid (c6)	acetovanillone
2-methylnaphthalene	9-methylantracene	heptanoic acid (c7)	dodecanoic (lauric) acid (c12)
1-methylnaphthalene	Anthraquinone	me-malonic (d-c3)	phthalic acid
Biphenyl	3,6-dimethylphenanthrene	guaiacol	levoglucosan
2-Methylbiphenyl	A-dimethylphenanthrene	benzoic acid	syringaldehyde
1+2ethylnaphthalene	B-dimethylphenanthrene	octanoic acid (c8)	tridecanoic acid (c13)
2,6+2,7-dimethylnaphthalene	C-dimethylphenanthrene	glycerol	isophthalic acid
1,3+1,6+1,7dimethylnaphth	D-dimethylphenanthrene	maleic acid	azelaic acid (d-c9)
1,4+1,5+2,3-dimethylnaphth	E-dimethylphenanthrene	succinic acid (d-c4)	myristoleic acid
Acenaphthylene	Fluoranthene	4-me-guaiacol	myristic acid (c14)
1,2-dimethylnaphthalene	1-MeFl+C-MeFl/Py	me-succinic acid (d-c4)	sebacic acid (d-c10)
3-Methylbiphenyl	Pyrene	o-toluic	pentadecanoic acid (c15)
Acenaphthene	9-Anthraaldehyde	picolinic acid	undecanedioic acid (d-c11)
4-Methylbiphenyl	Retene	m-toluic	palmitoleic acid
Dibenzofuran	B-MePy/MeFl	nonanoic acid (c9)	palmitic acid (c16)
A-trimethylnaphthalene	C-MePy/MeFl	p-toluic	isostearic acid
B-trimethylnaphthalene	D-MePy/MeFl	3-, 6-methylpicolinic acid	heptadecanoic acid (c17)
C-trimethylnaphthalene	4-methylpyrene	2,6-dimethylbenzoic acid	1,11-undecanedicarboxylic acid (d-c13)
E-trimethylnaphthalene	1-methylpyrene	4-ethyl-guaiacol	oleic acid
F-trimethylnaphthalene	2,3-Benzofluorene	syringol	elaidic acid
2,3,5+I-trimethylnaphthalene	Benzonaphthothiophene	glutaric acid (d-c5)	stearic acid (c18)
J-trimethylnaphthalene	Benzo(c)phenanthrene	2-methylglutaric (d-c5)	1,12-dodceanedicarboxylic acid (d-c14)
2,4,5,-trimethylnaphthalene	Benz(a)anthracene	2,5-dimethylbenzoic acid	nonadecanoic acid (c19)
Fluorene	Chrysene	3-methylglutaric acid (d-c5)	dehydroabietic acid
1,4,5-trimethylnaphthalene	Benzanthrone	2,4-dimethylbenzoic acid	eicosanoic acid (c20)
A-methylfluorene	Benz(a)anthracene-7,12-dione	3,5-dimethylbenzoic acid	abietic acid
1-methylfluorene	5+6-methylchrysene	2,3-dimethylbenzoic acid	heneicosanoic acid (c21)
B-methylfluorene	7-methylbenz(a)anthracene	decanoic acid (c10)	cholesterol
9-fluorenone	1,4-chrysenequinone	4-allyl-guaiacol (eugenol)	b-sitosterol
Phenanthrene	Benzo(b+j+k)fluoranthene	4-methyl-syringol	
Anthracene	BeP	3,4-dimethylbenzoic acid	
Xanthone	BaP	hexanedioic (adipic) acid (d-c6)	
Acenaphthenequinone	Perylene	trans-2-decenoic acid	
A-methylphenanthrene	7-methylbenzo(a)pyrene	cis-pinonic acid	
2-methylphenanthrene	9,10-dihydrobenzo(a)pyrene-7(8H)-one	3-methyladipic acid (d-c6)	
Perinaphthenone	Indeno[123-cd]pyrene	4-formyl-guaiacol (vanillin)	
B-methylphenanthrene	Dibenzo(ah+ac)anthracene	undecanoic acid (c11)	
C-methylphenanthrene	Benzo(ghi)perylene	isoeugenol	
1-methylphenanthrene	Coronene	heptanedioic (pimelic) acid (d-c7)	

Compound List: High MW Alkanes, Hopanes, & Steranes

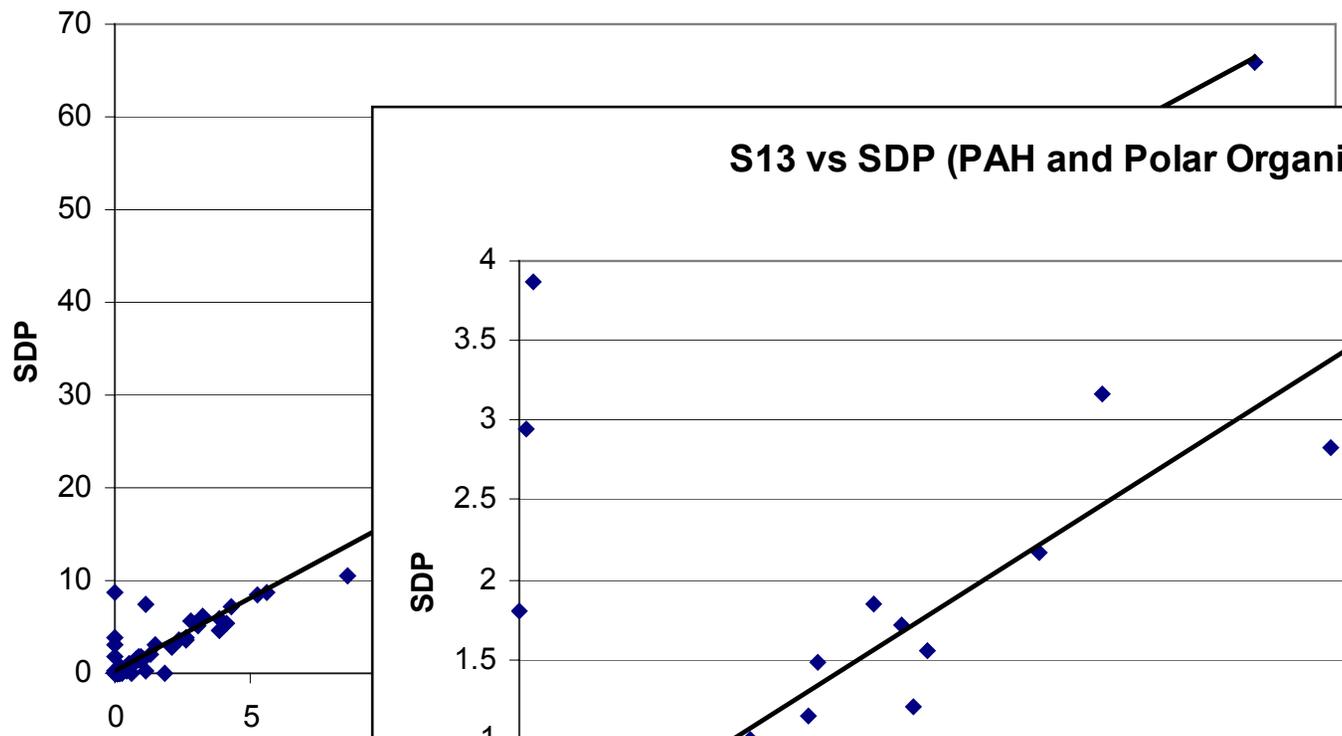
norfarnesane
a-3-methyl-1-hexylcyclohexane
a-4-methyl-1-hexylcyclohexane
a-2-methyl-1-hexylcyclohexane
b-3-methyl-1-hexylcyclohexane
b-4-methyl-1-hexylcyclohexane
b-2-methyl-1-hexylcyclohexane
heptylcyclohexane
farnesane
octylcyclohexane
nonylcyclohexane
norpristane
hexadecane
heptadecane
decylcyclohexane
pristane
undecylcyclohexane
octadecane
nonadecane
phytane
dodecylcyclohexane
tridecylcyclohexane
tetradecylcyclohexane
eicosane
heneicosane
pentadecylcyclohexane
hexadecylcyclohexane
tricosane
heptadecylcyclohexane
octadecylcyclohexane

tetracosane
pentacosane
hexacosane
nonadecylcyclohexane
eicosylcyclohexane
heptacosane
octacosane
nonacosane
triacontane
hentriacontane
dotriacontane
tritriacontane
tetratriacontane
pentatriacontane
hexatriacontane

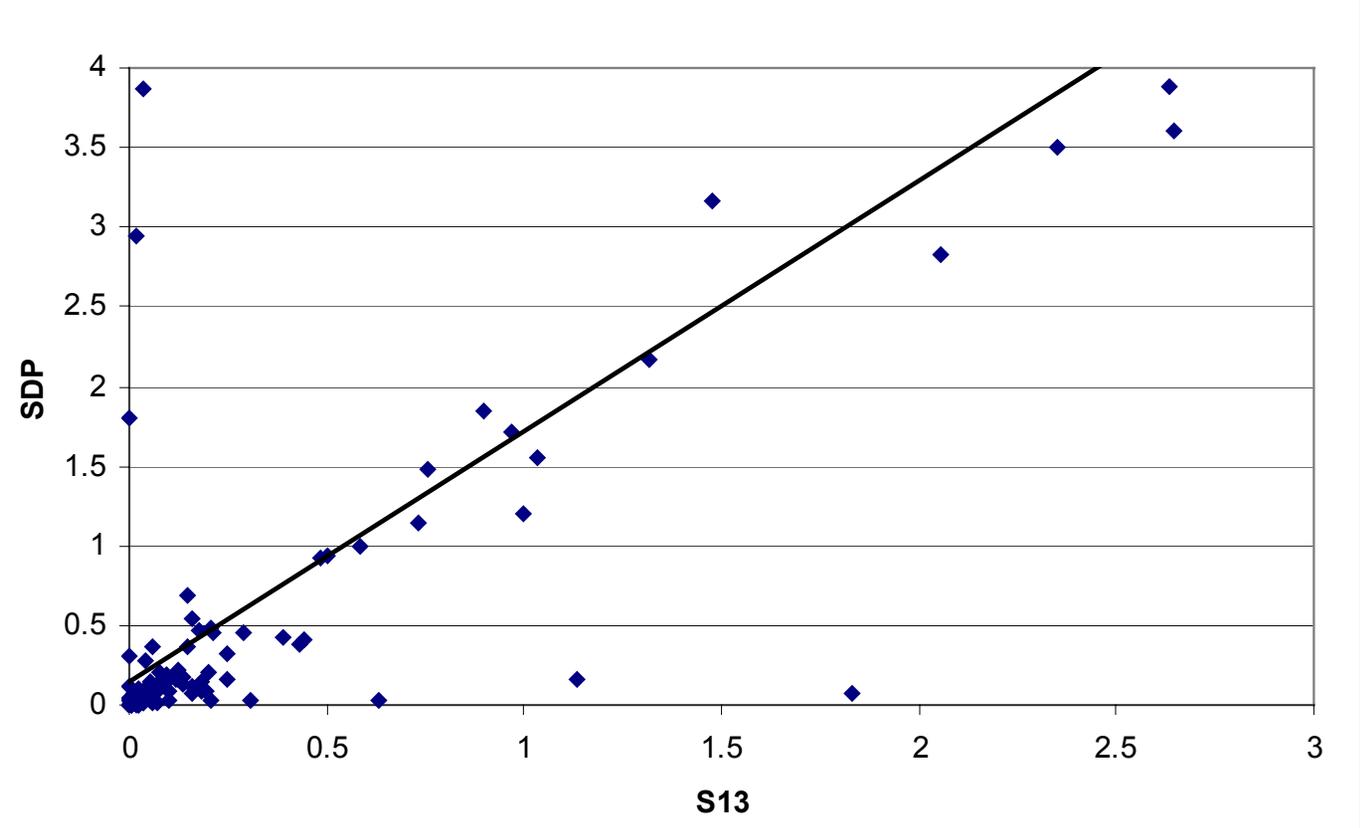
C27-20S-13 β (H),17a(H)-diasterane
C27-20R5a(H),14 β (H)-cholestane
C27-20R5a(H),14a(H),17a(H)-cholestane&C29-20S13 β (H),17a(H)-diasterane
C28-20S5a(H),14 β (H),17 β (H)-ergostane&C29-20R-13a(H),17 β (H)-diasterane
C28-20R5a(H),14a(H),17a(H)-ergostane
17a(H),21 β (H)-30-Norhopane
17 β (H),21a(H)-30-norhopane
17a(H),21 β (H)-Hopane
17 β (H),21 β (H)-Hopane
22S-17a(H),21 β (H)-30,31-Bishomohopane
22S-17a(H),21 β (H)-30,31,32-Trishomohopane

Sacramento PAH and Polar Organic Species Correlation

S13 vs SDP (PAH and Polar Organics) $y = 1.5733x + 0.1411$
 $R^2 = 0.9716$



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 $R^2 = 0.9716$



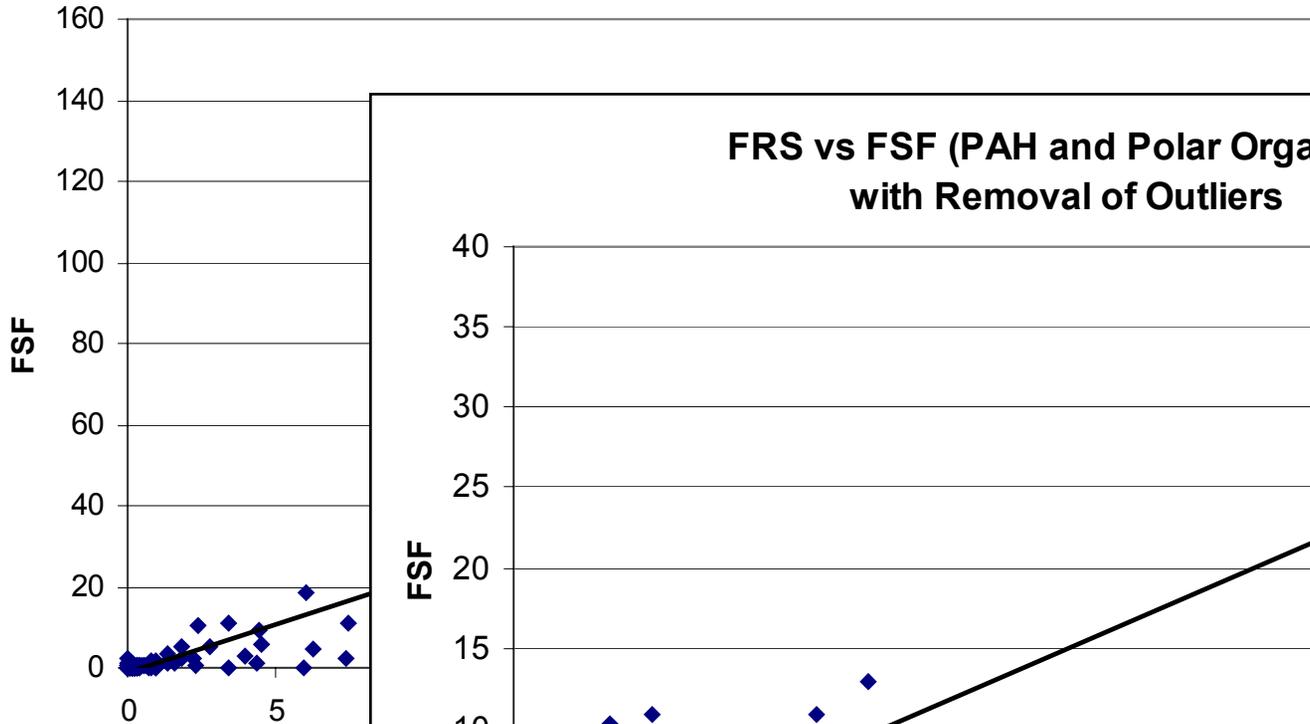
n= 140 species

Fresno PAH and Polar Organic Species Correlation

FRS vs FSF (PAH & Polar Organics)

$$y = 2.3862x - 0.9817$$

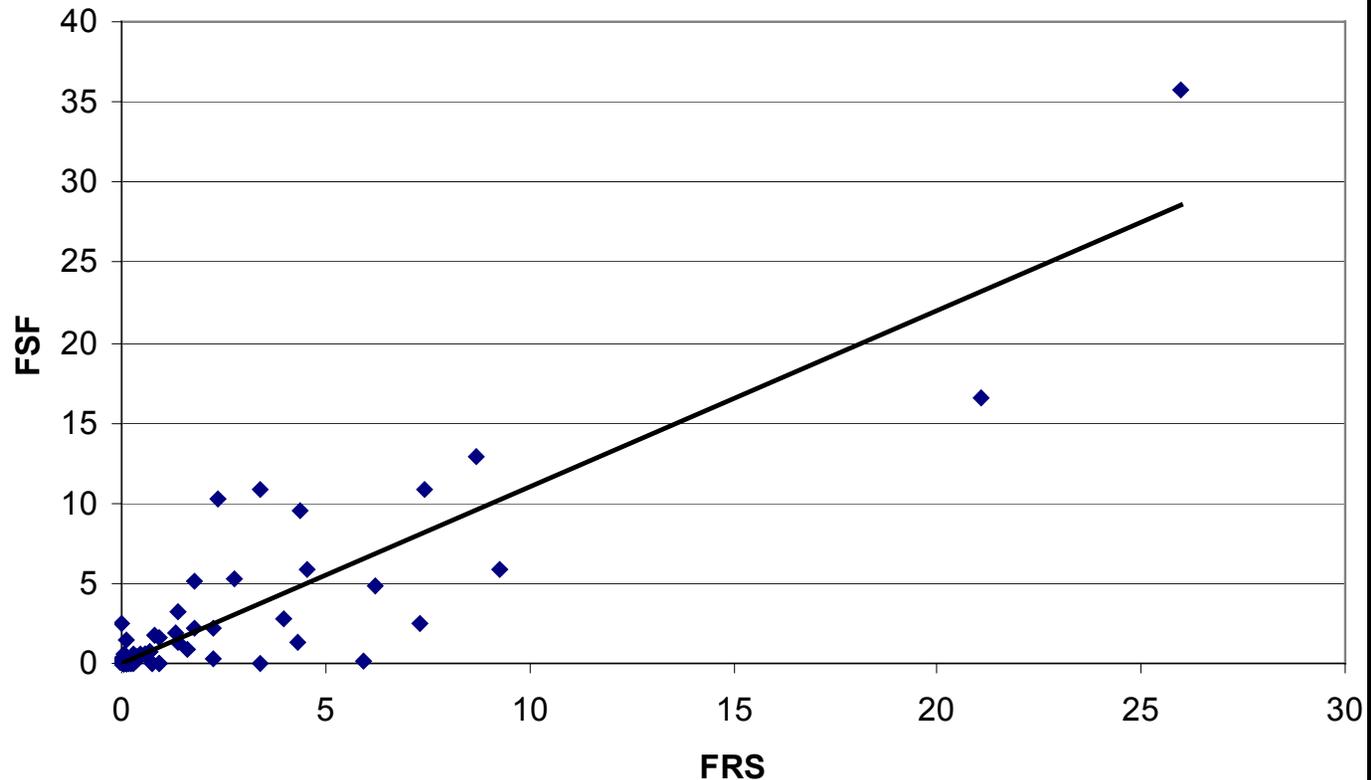
$$R^2 = 0.7392$$



FRS vs FSF (PAH and Polar Organics)
with Removal of Outliers

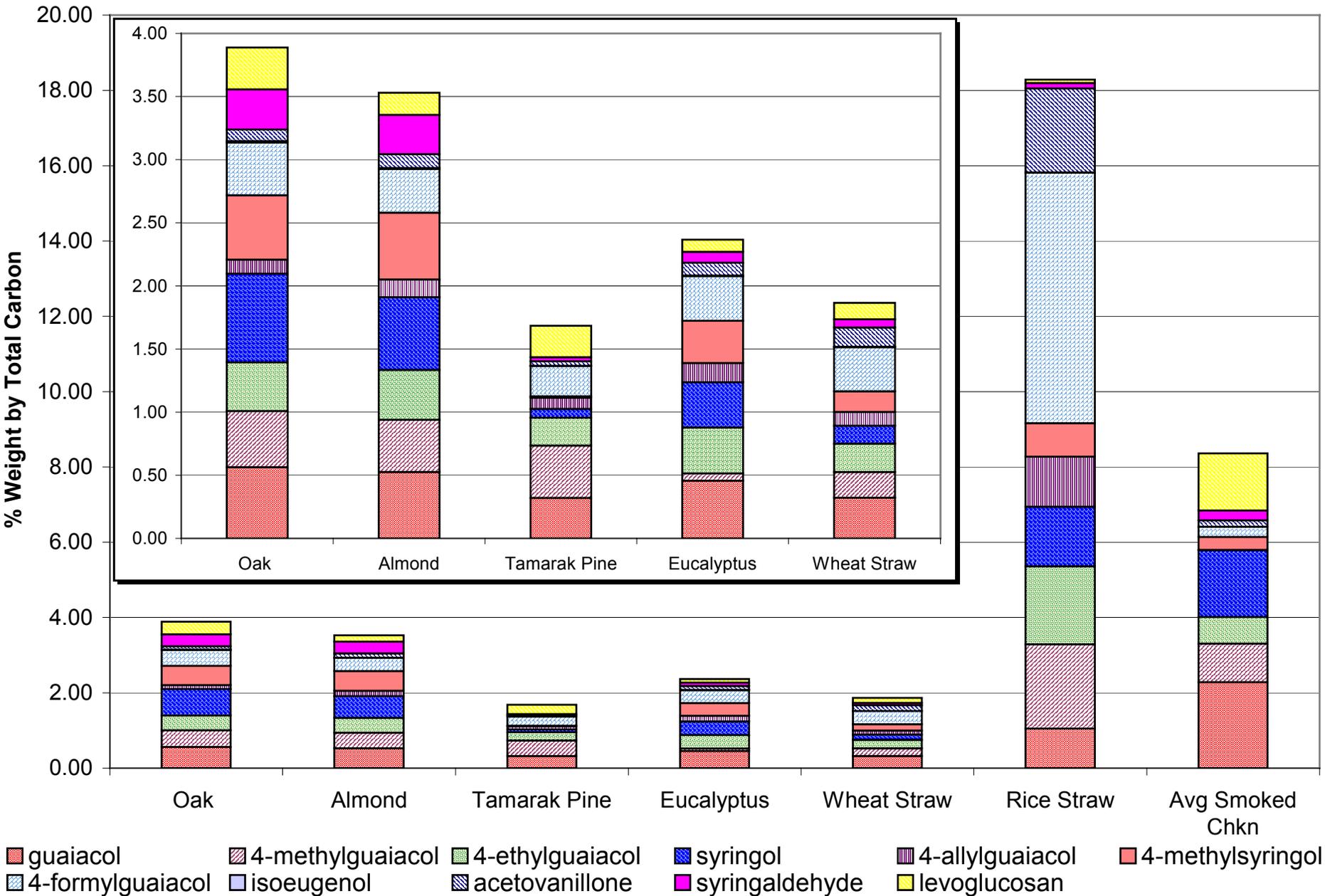
$$y = 1.1001x + 0.0271$$

$$R^2 = 0.8098$$



n= 140 species

Biomass Combustion Characterization

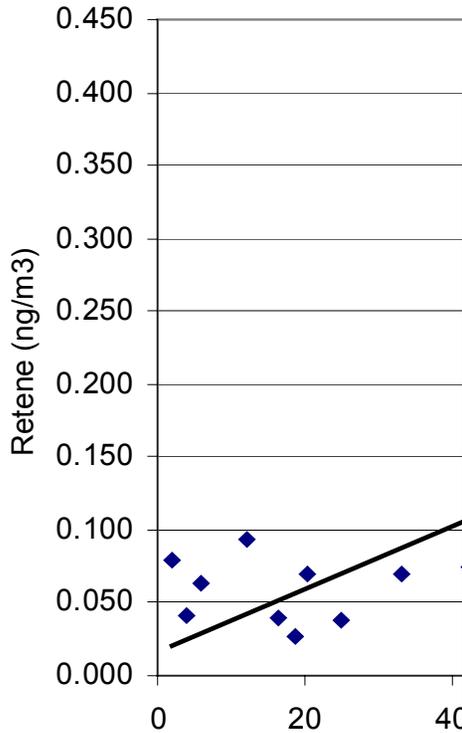


Biomass Combustion Tracers

Levoglucosan vs. Retene

$$y = 0.0022x + 0.0164$$

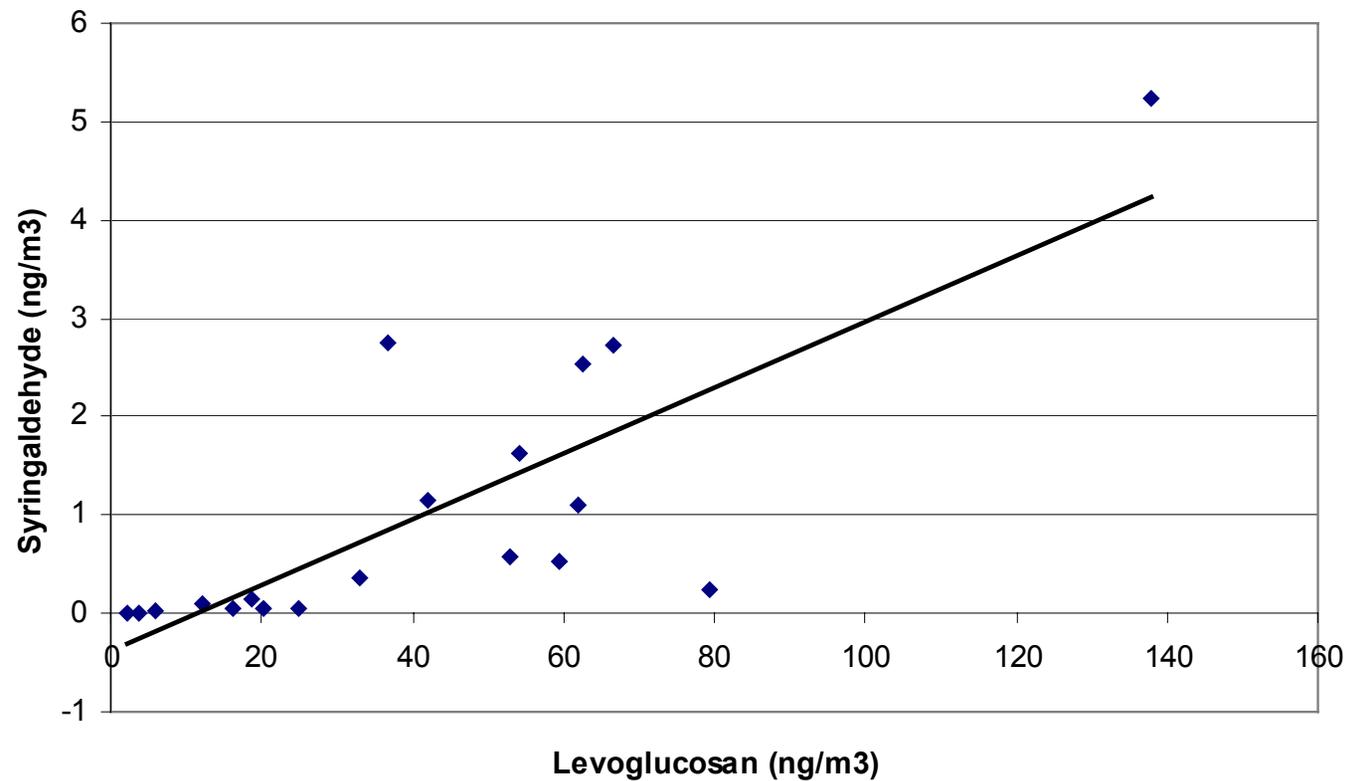
$$R^2 = 0.6127$$



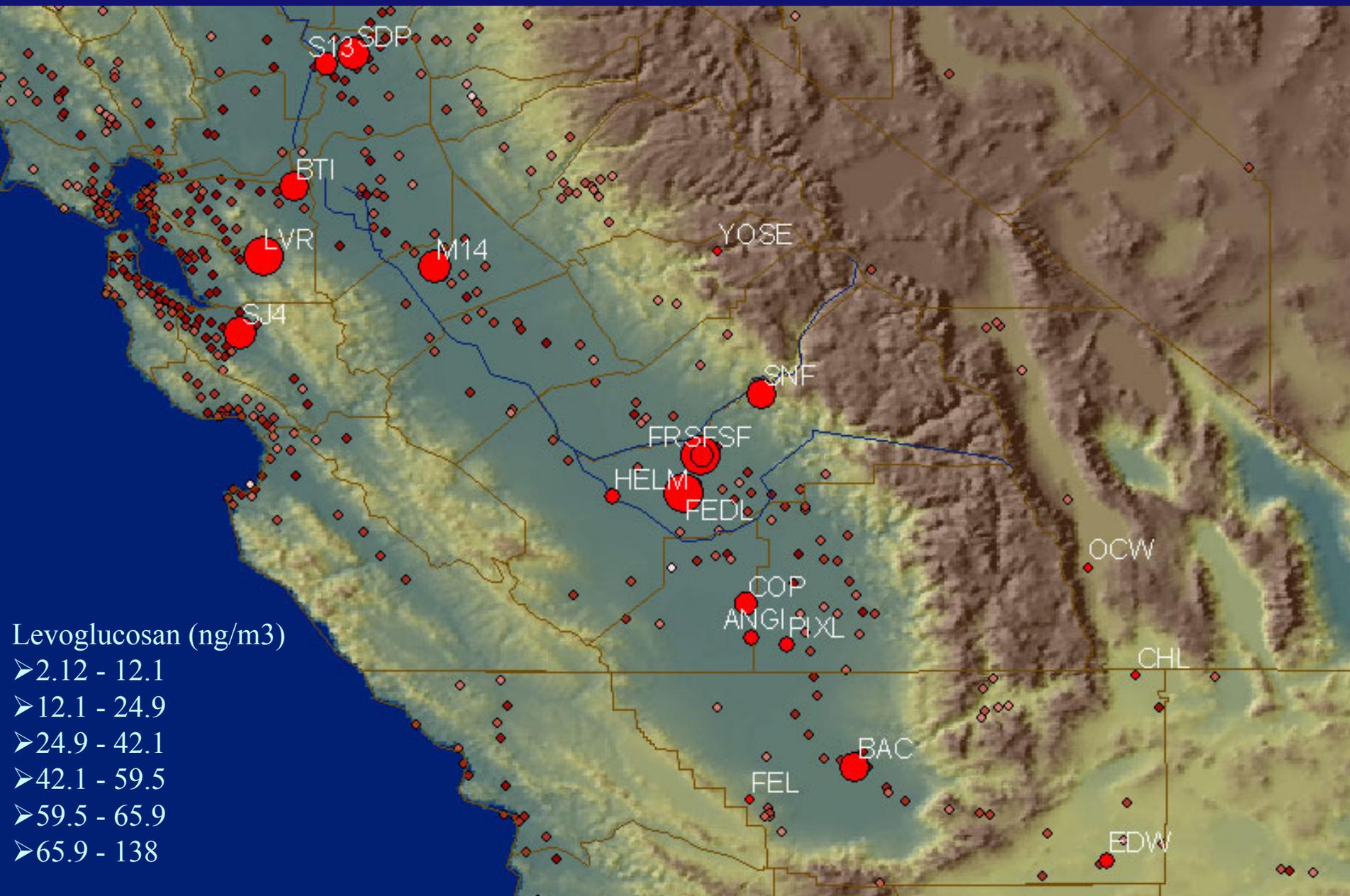
Levoglucosan vs Syringaldehyde

$$y = 0.0334x - 0.3765$$

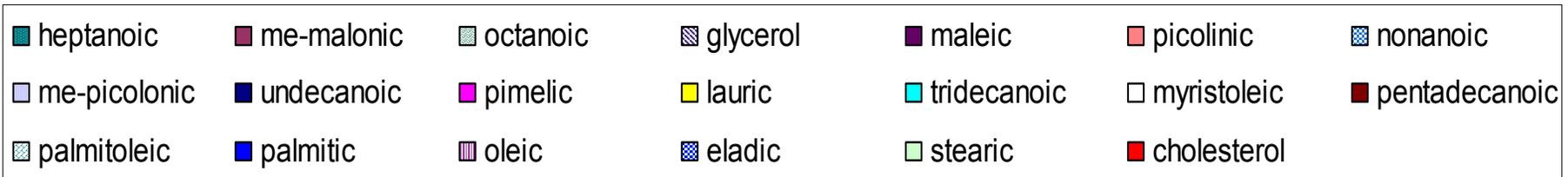
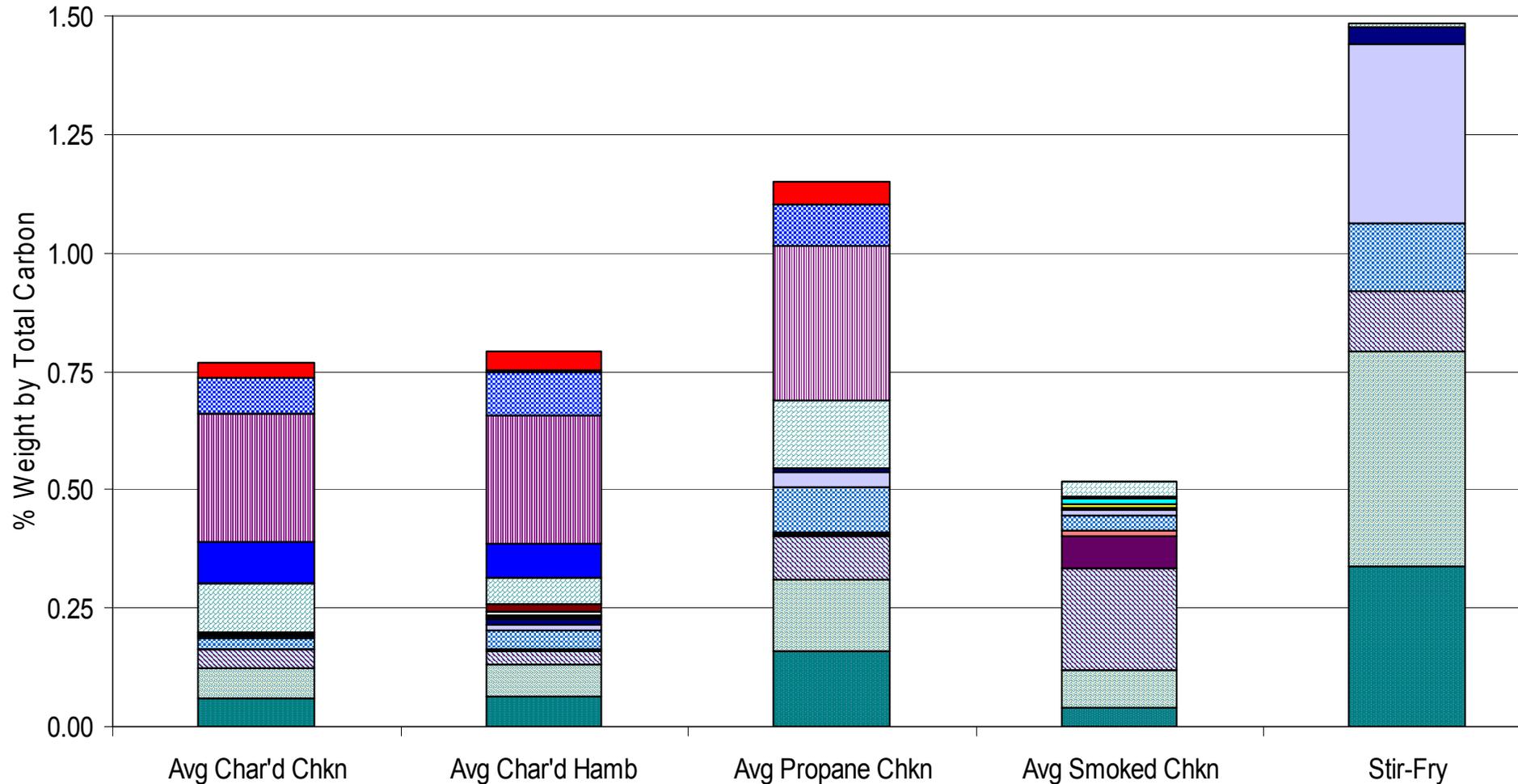
$$R^2 = 0.6304$$



Levoglucosan (ng/m³)



Meat Cooking Characterization

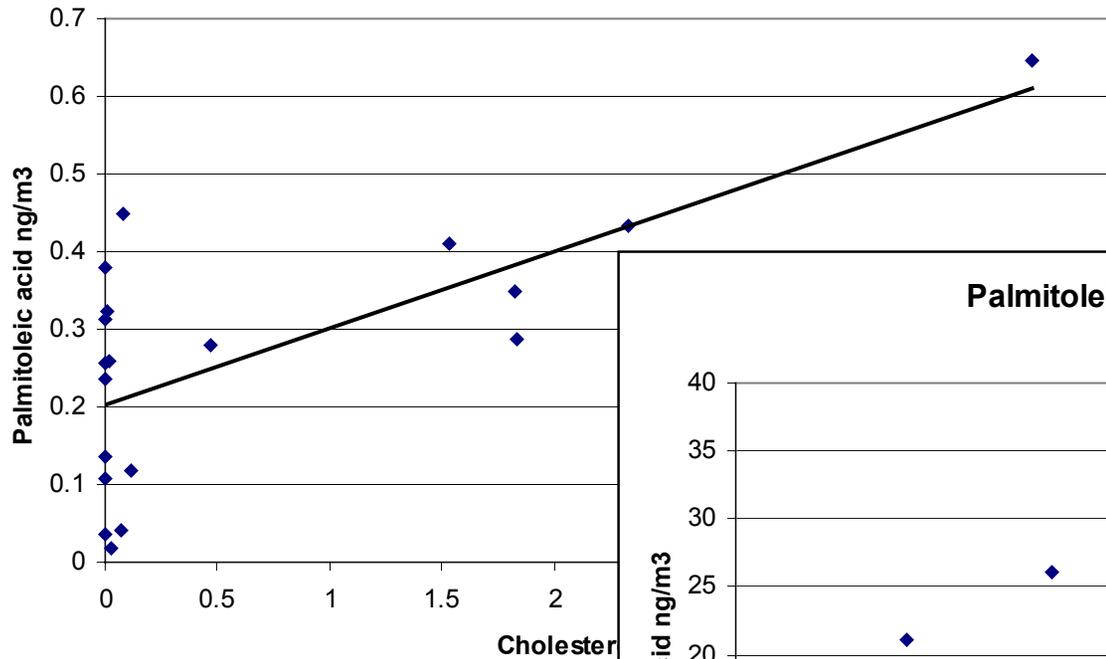


Meat Cooking Tracers

Cholesterol vs Palmitoleic Acid

$$y = 0.0988x + 0.2025$$

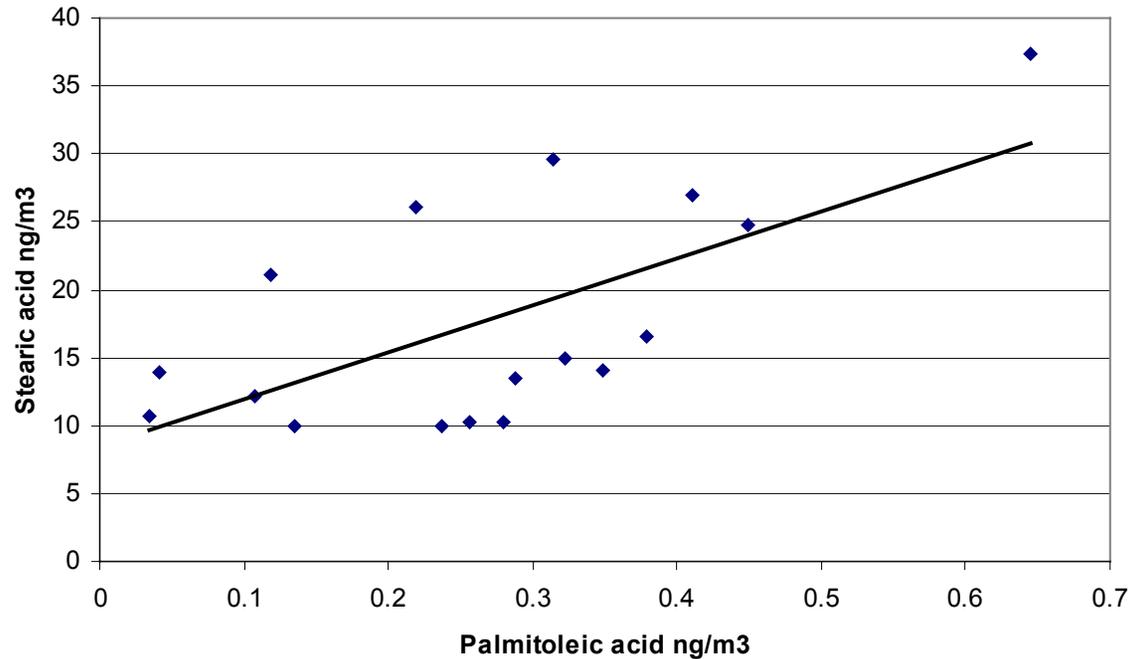
$$R^2 = 0.4787$$



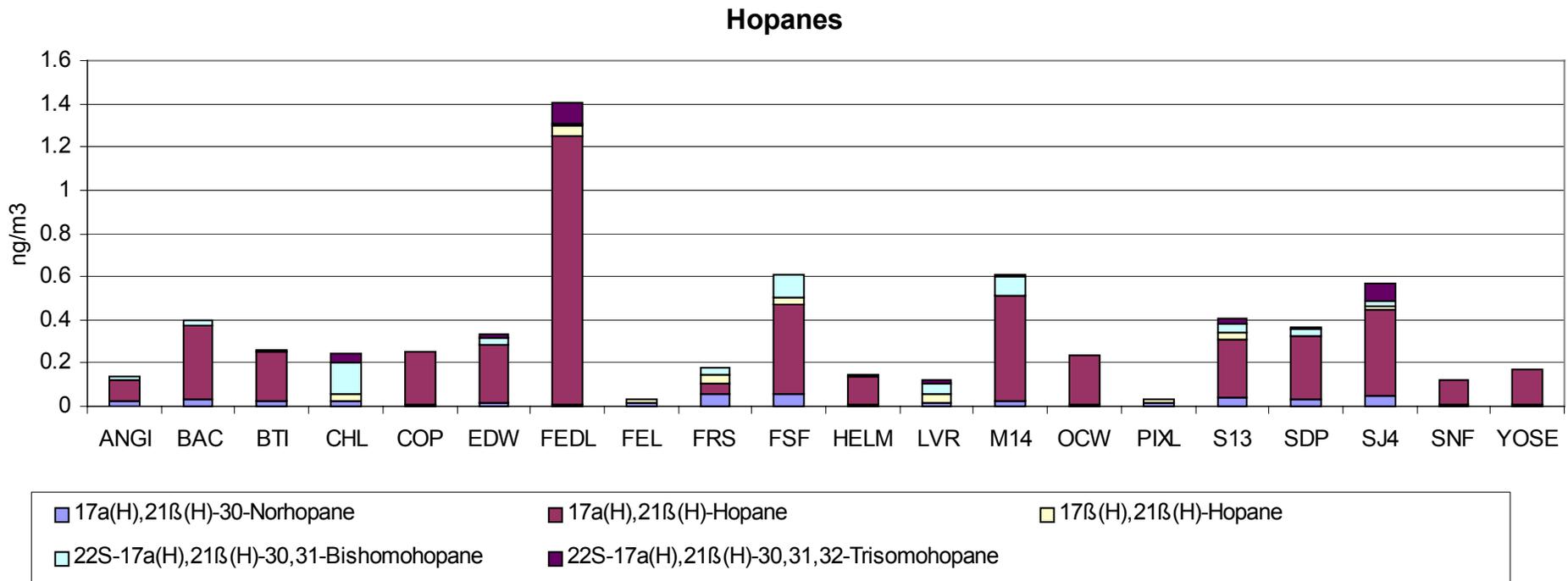
Palmitoleic Acid vs Stearic Acid

$$y = 34.57x + 8.4536$$

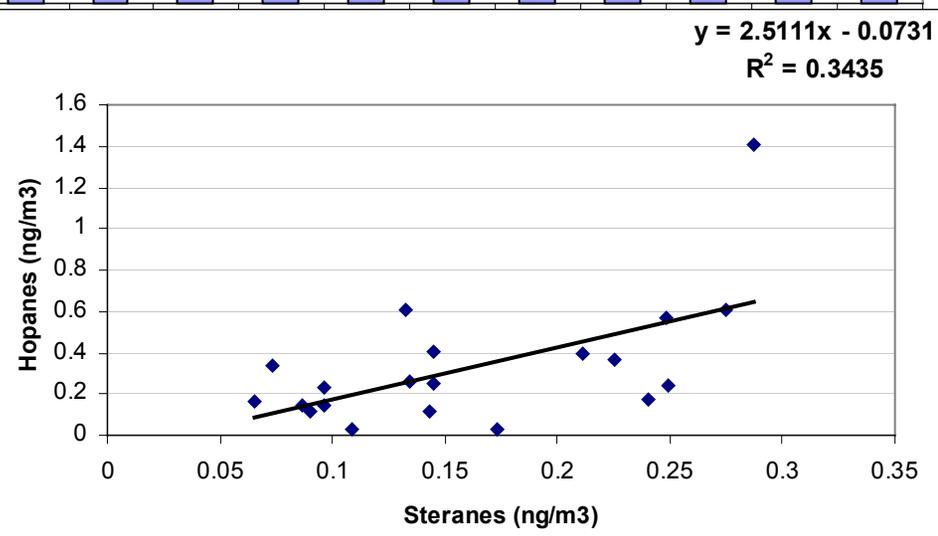
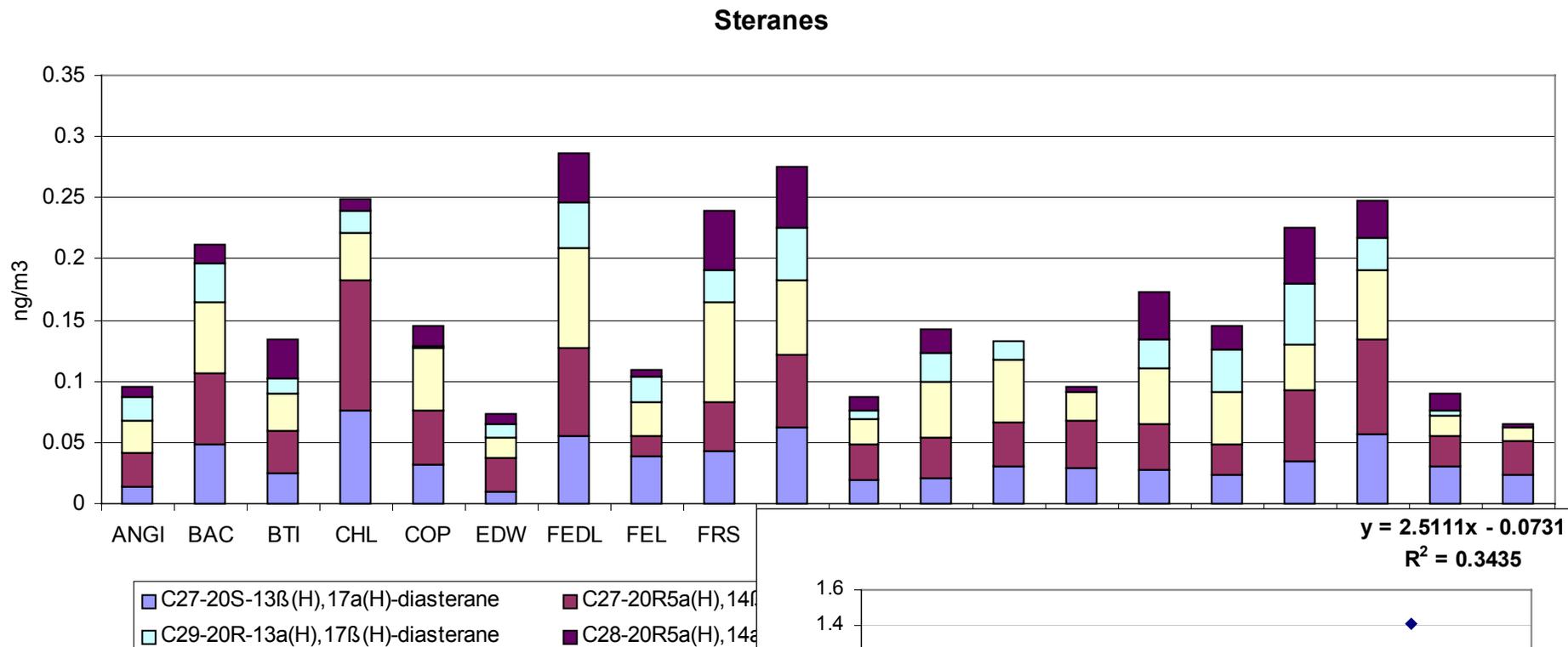
$$R^2 = 0.4241$$



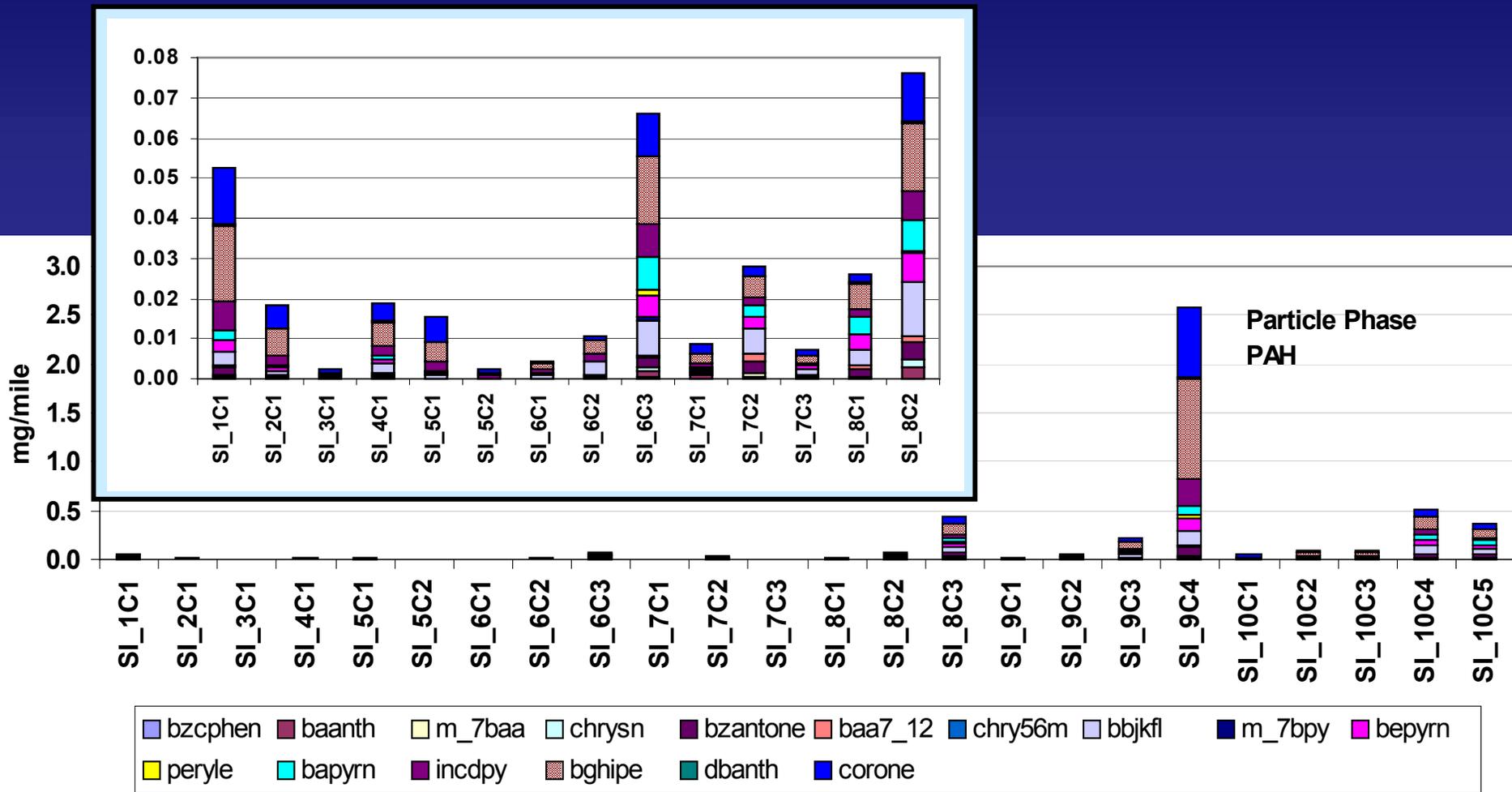
Vehicle Markers: Hopanes



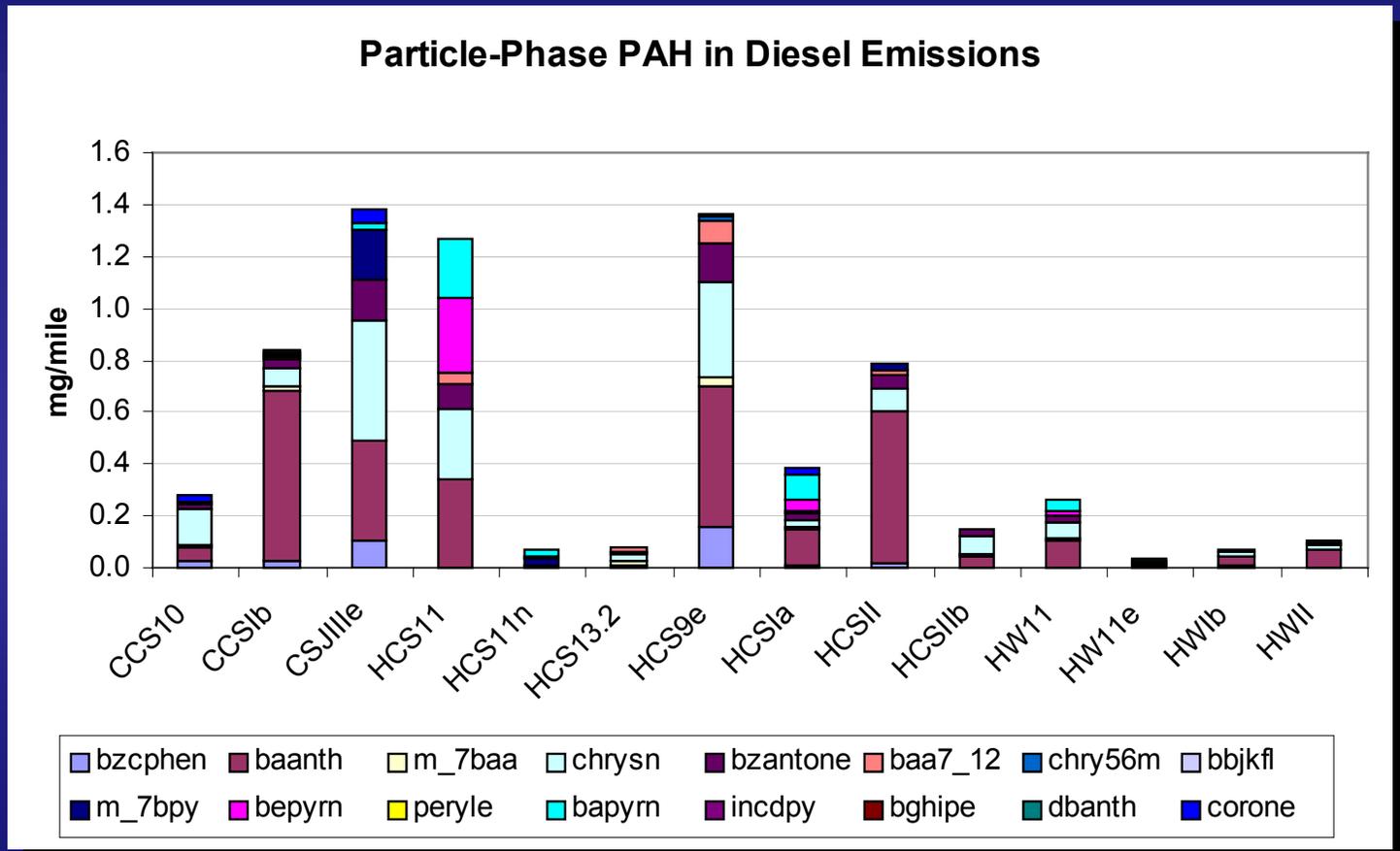
Vehicle Markers: Steranes



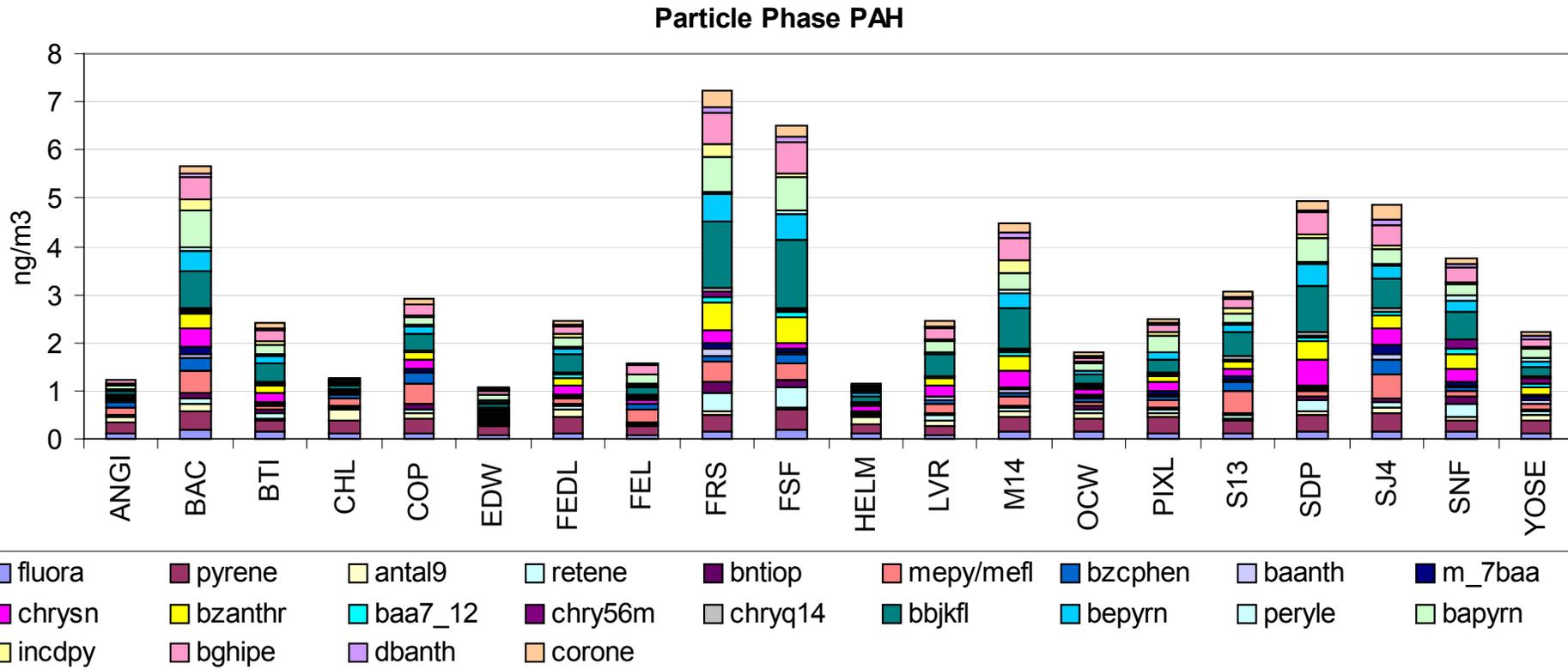
Spark Ignition Vehicle Characterization



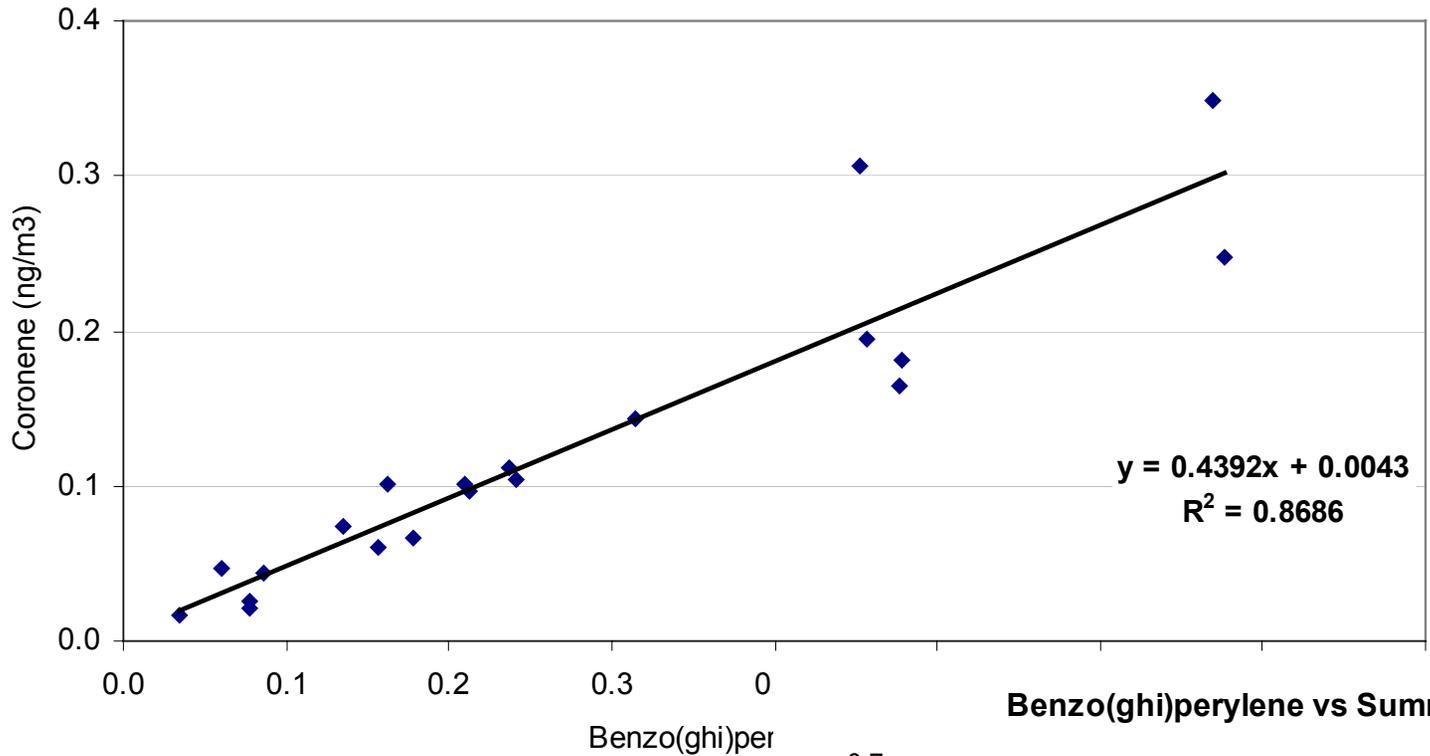
Compression Ignition Vehicle Characterization



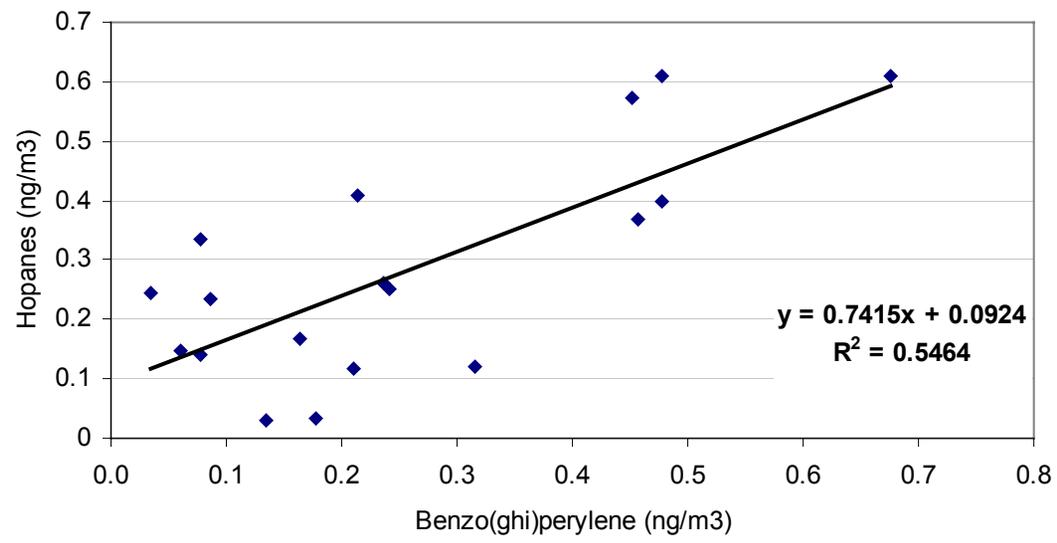
PAH Concentrations for Annual Average Sites



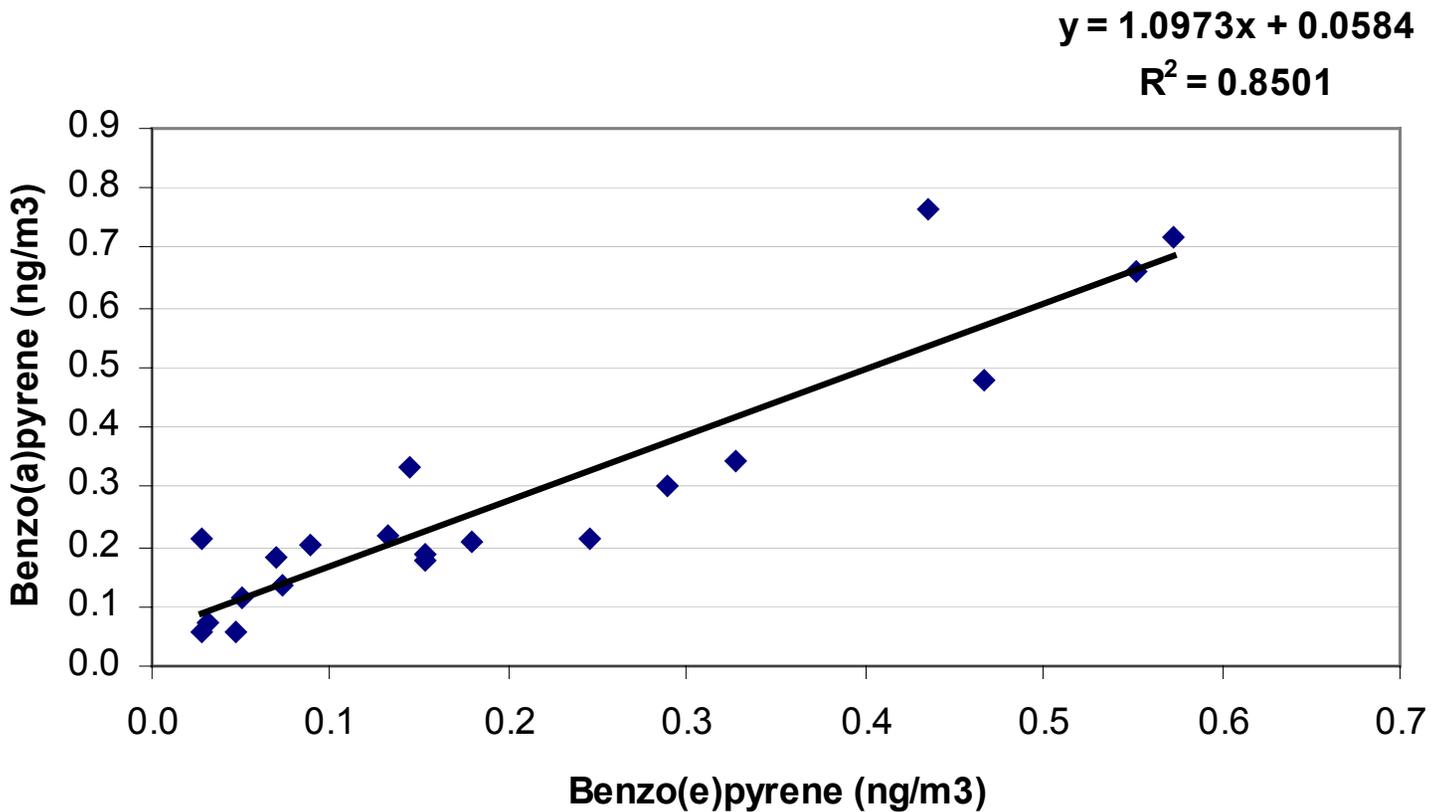
Benzo(ghi)perylene vs Coronene



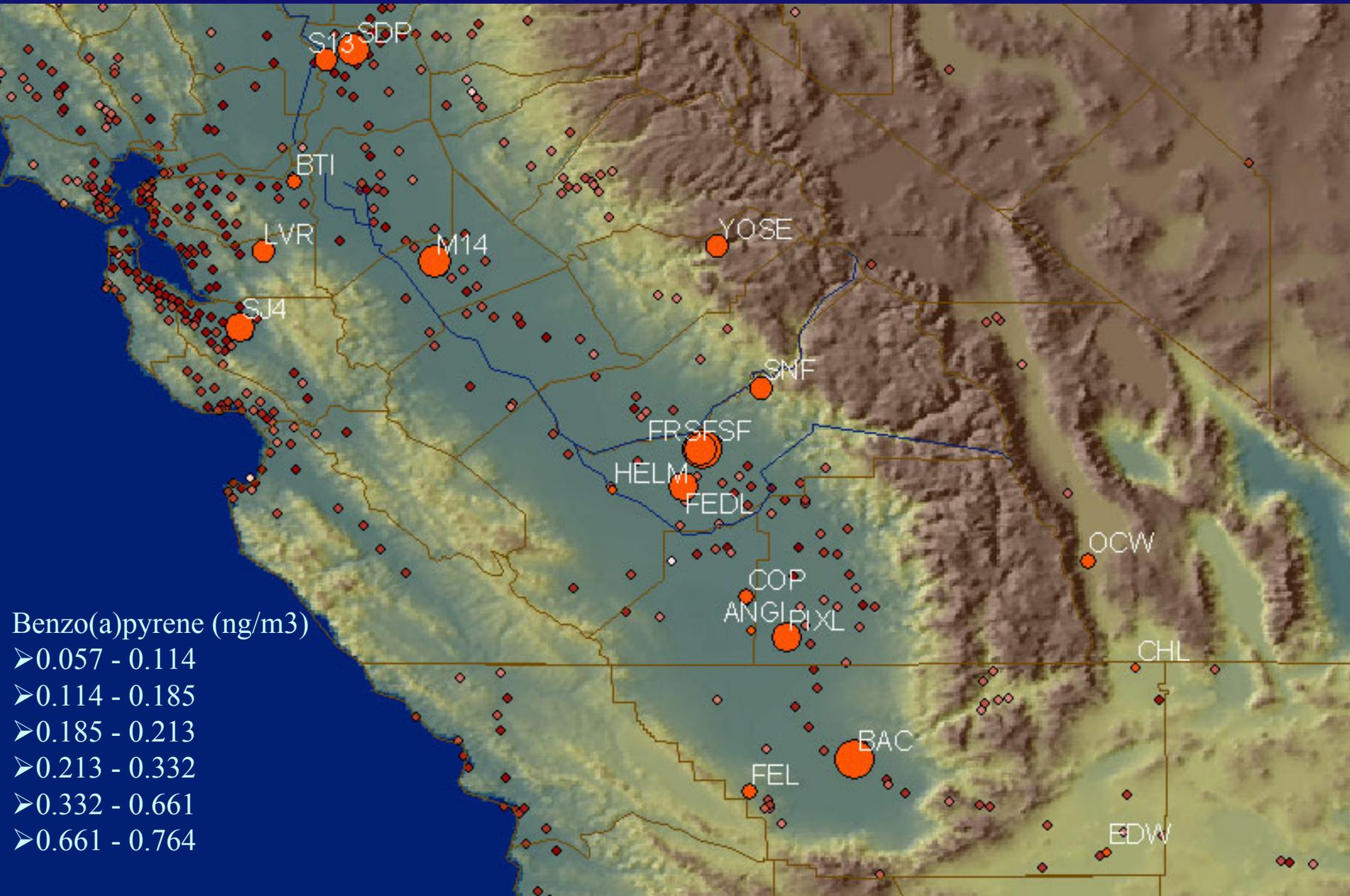
Benzo(ghi)perylene vs Summed Hopanes



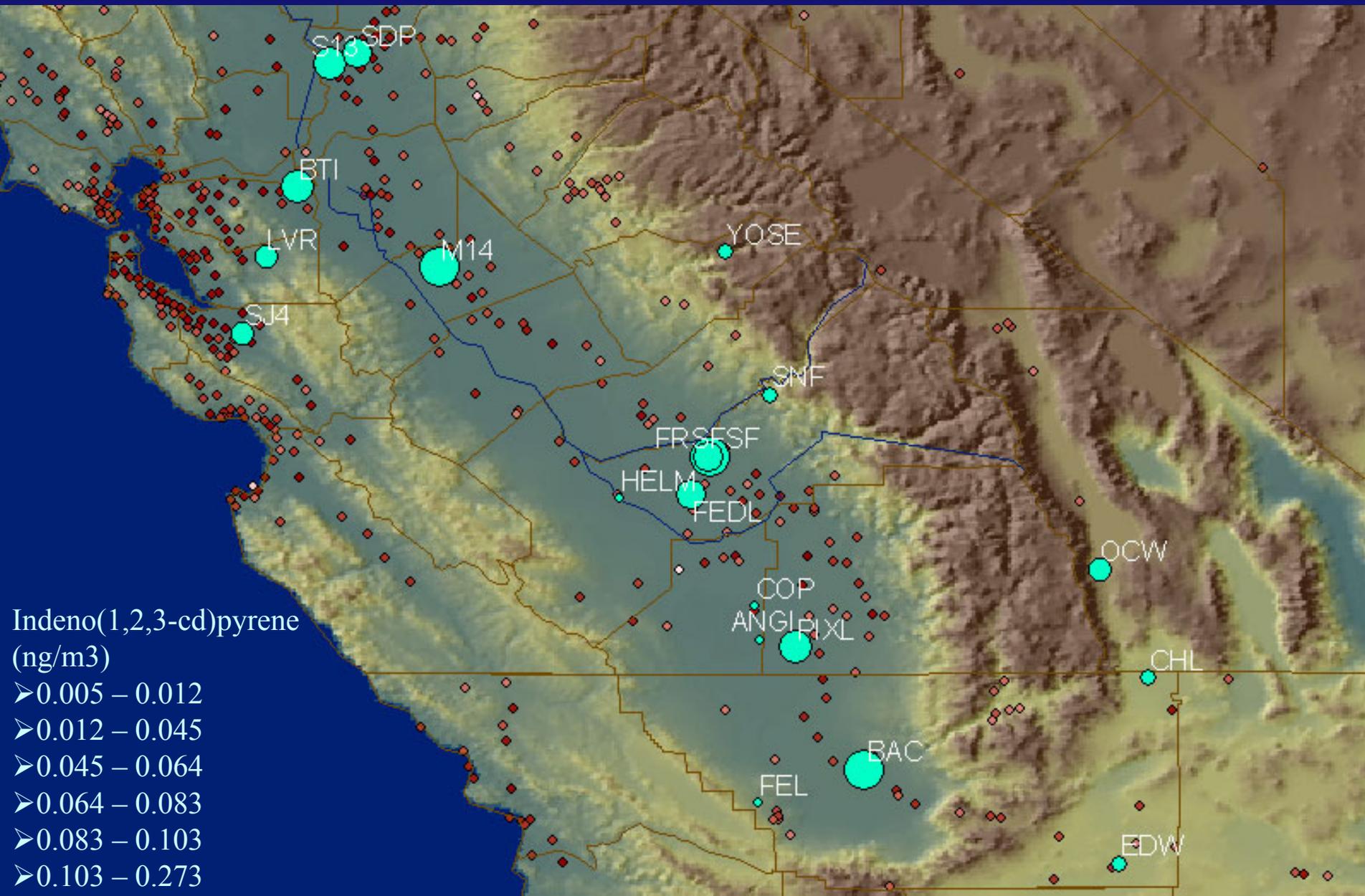
Benzo(e)pyrene vs Benzo(a)pyrene



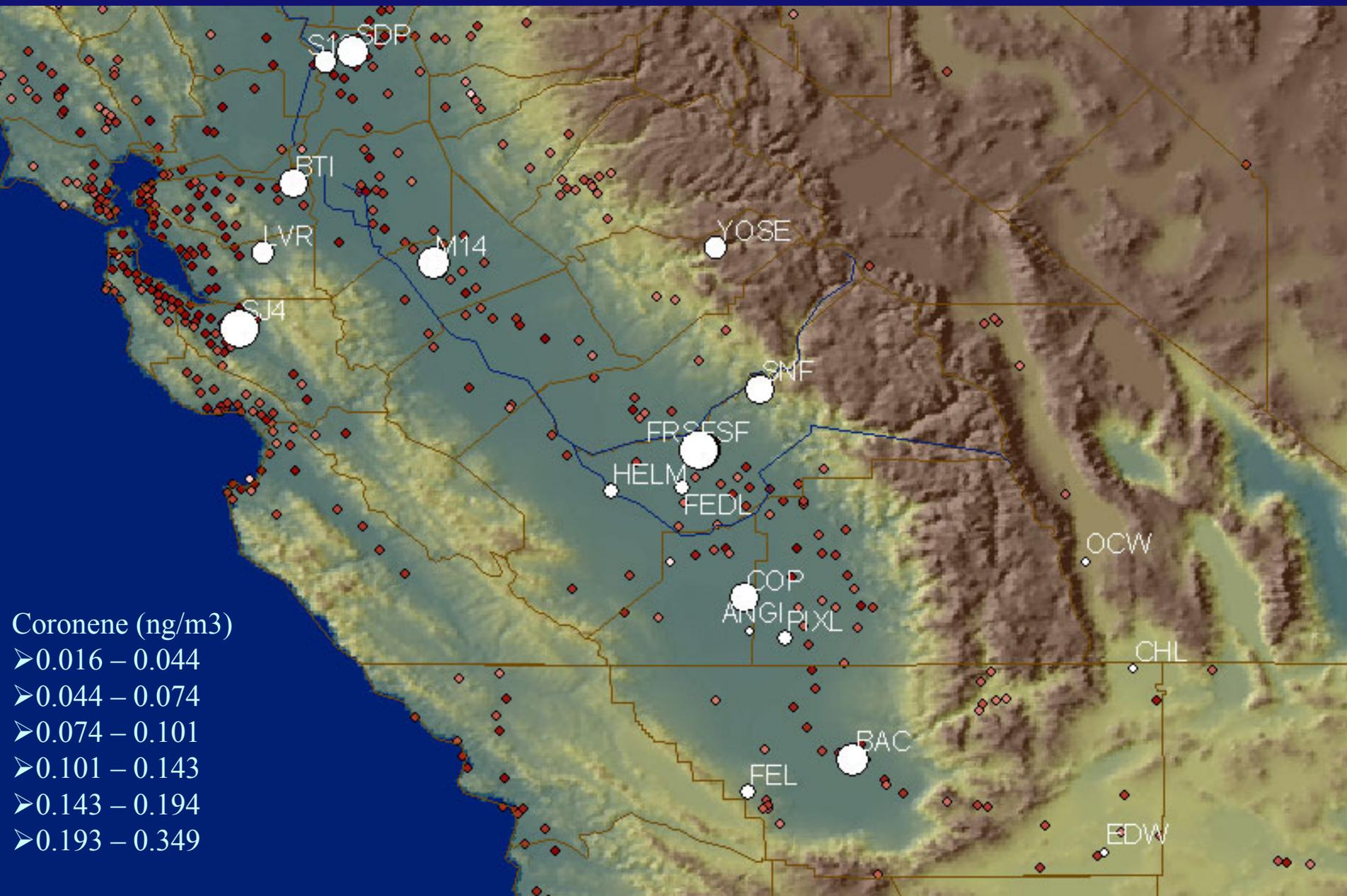
Benzo(a)pyrene (ng/m³)



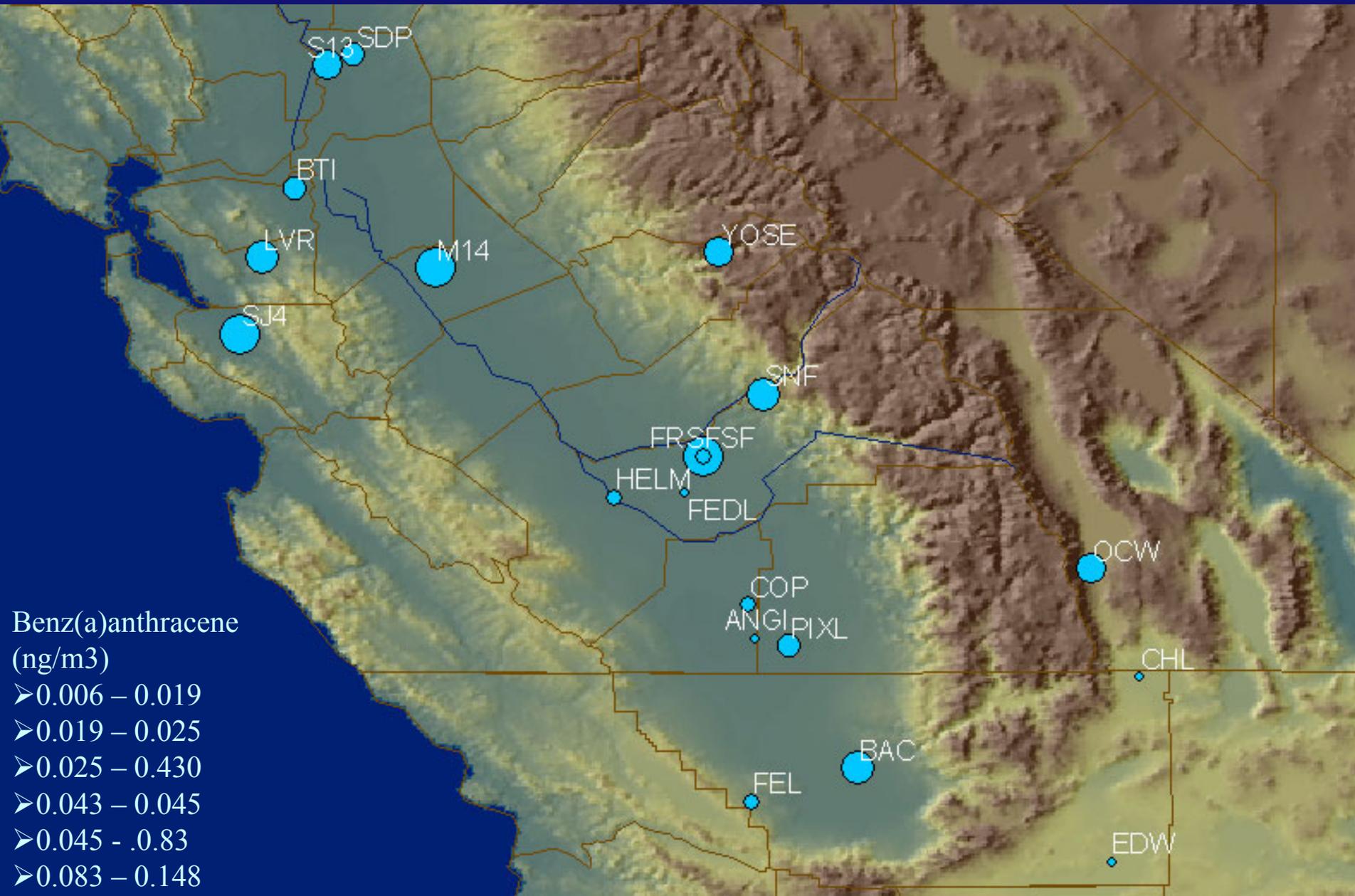
Indeno(1,2,3-cd)pyrene (ng/m³)



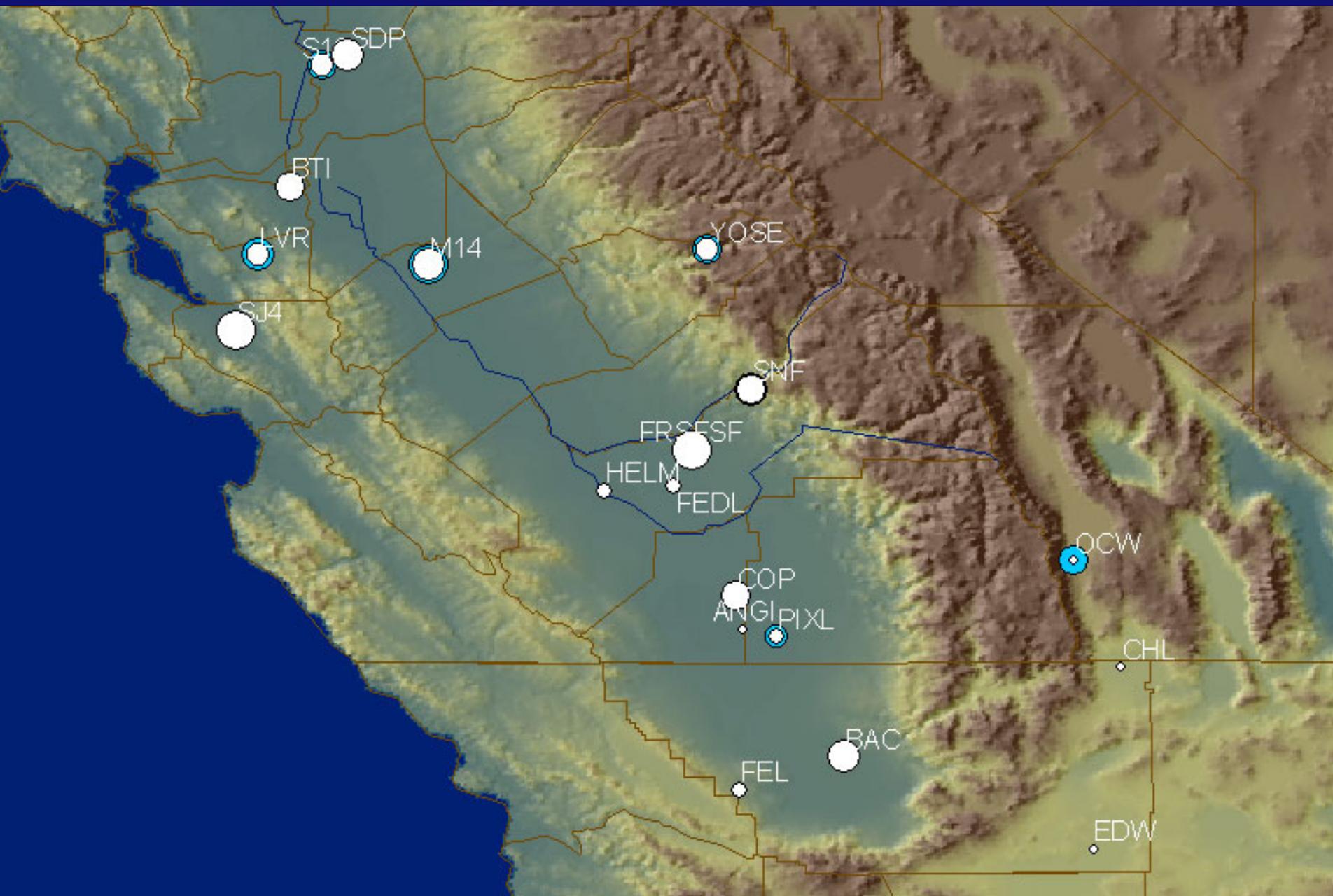
Coronene (ng/m³)



Benz(a)anthracene (ng/m³)



Benz(a)anthracene with Coronene Overlaid

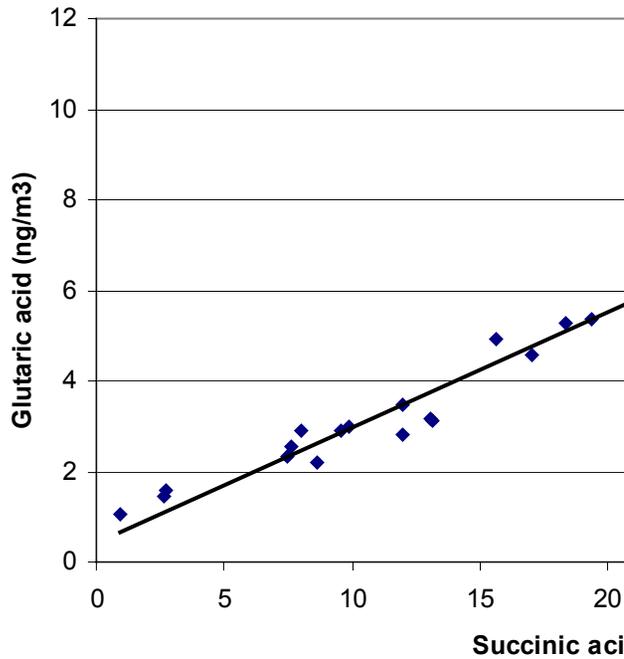


Di-alkanoic Acids

Succinic Acid vs Glutaric Acid

$$y = 0.2546x + 0.4202$$

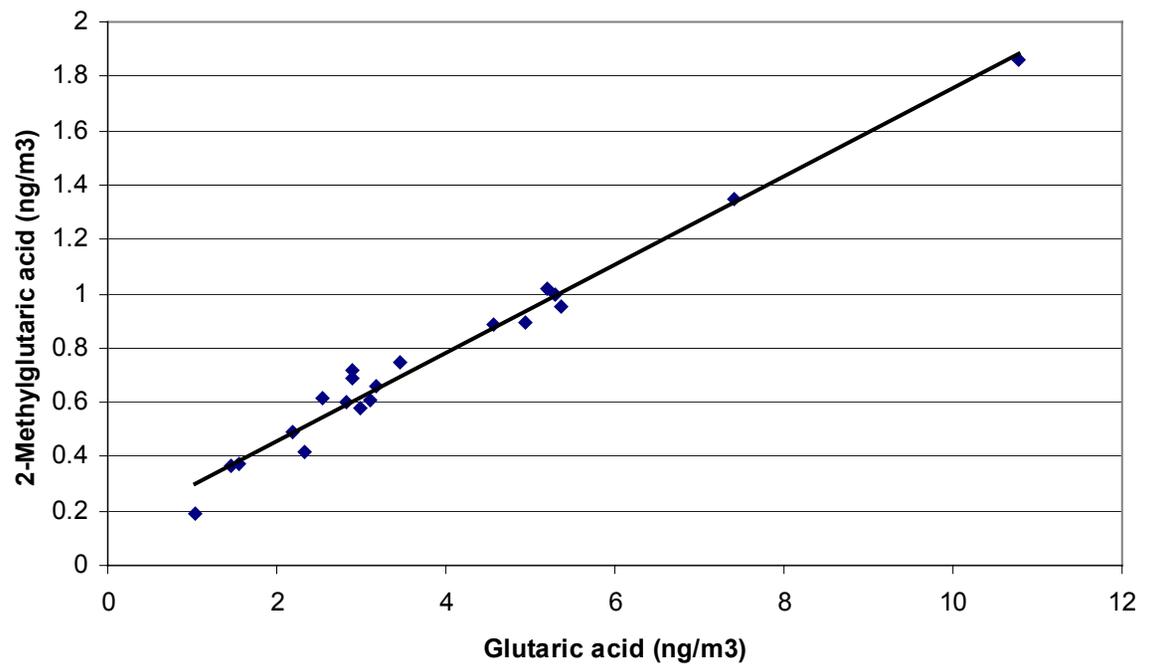
$$R^2 = 0.9302$$



Glutaric Acid vs 2-Methylglutaric Acid

$$y = 0.1626x + 0.1333$$

$$R^2 = 0.9782$$

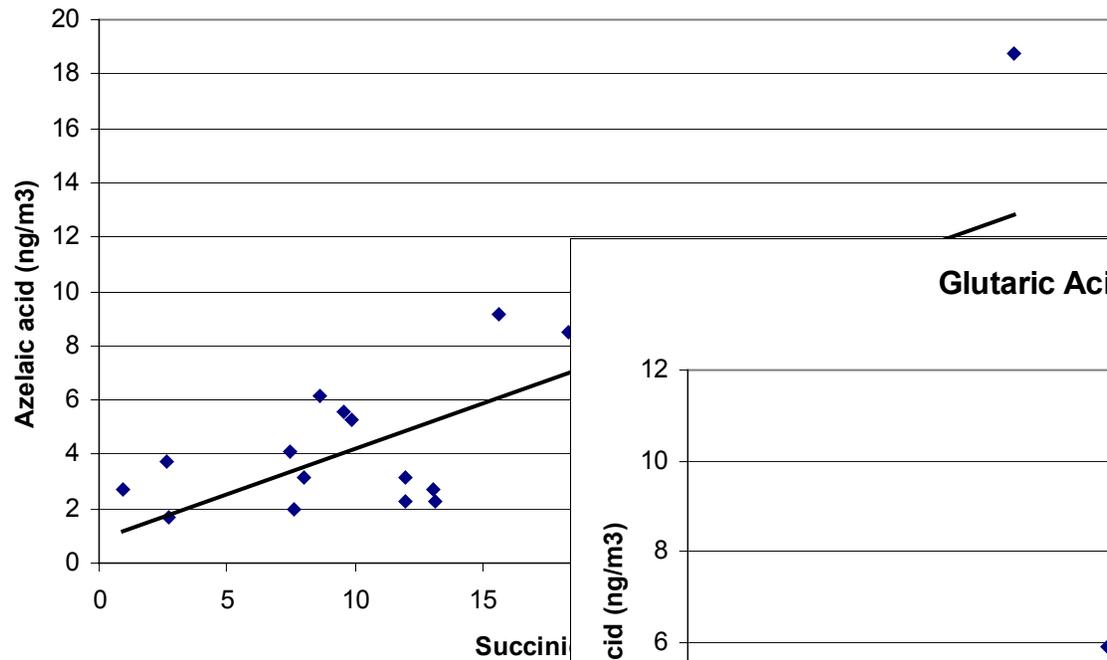


Di-acids

Succinic Acid vs Azelaic Acid

$$y = 0.3341x + 0.873$$

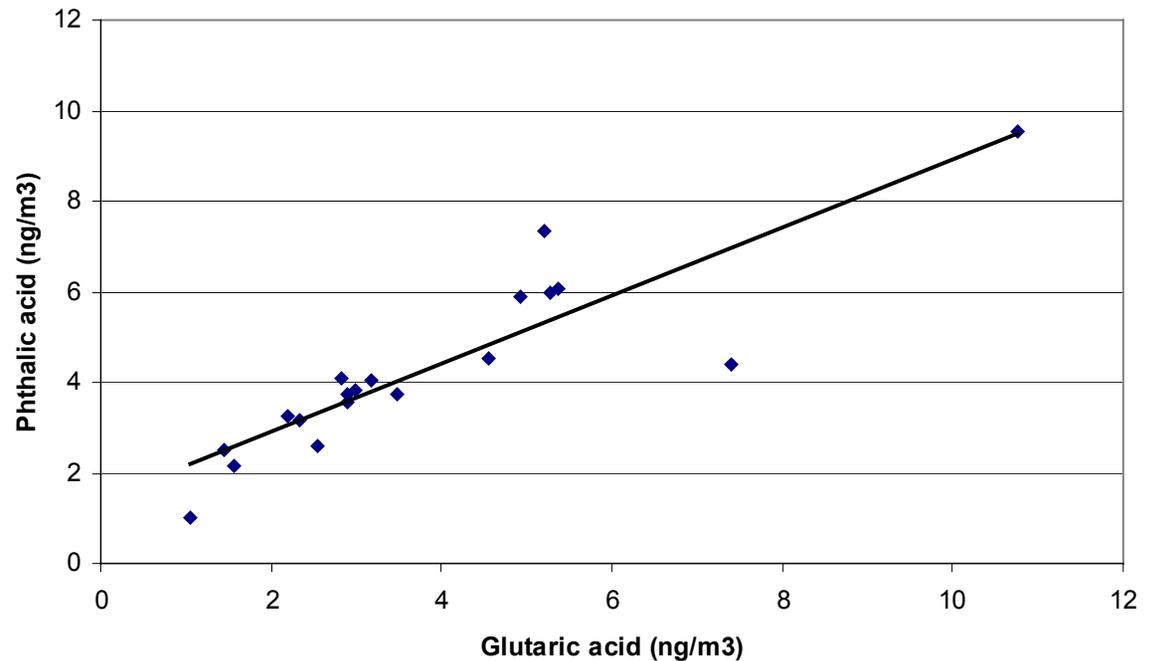
$$R^2 = 0.5505$$



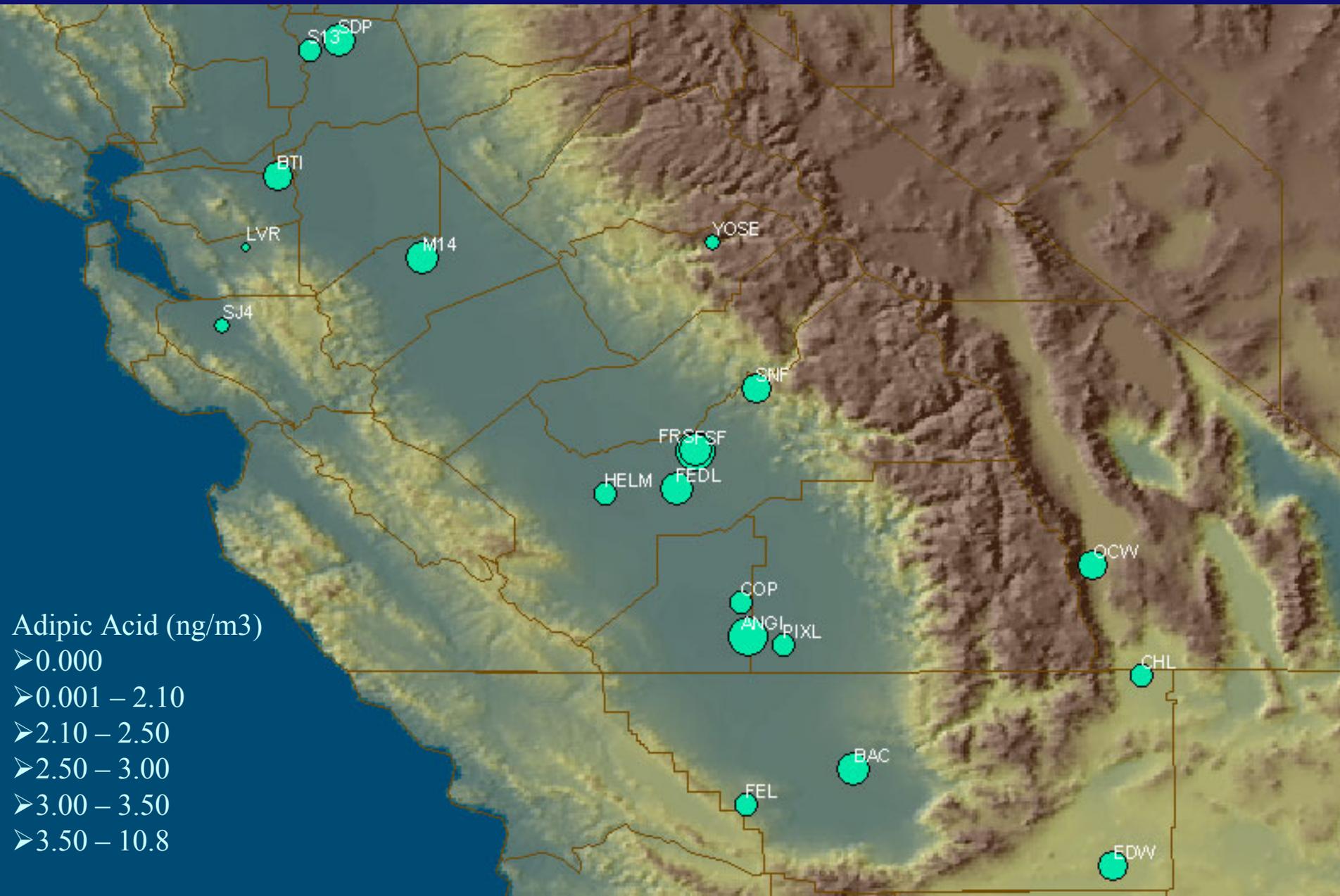
Glutaric Acid vs Phthalic Acid

$$y = 0.7526x + 1.4028$$

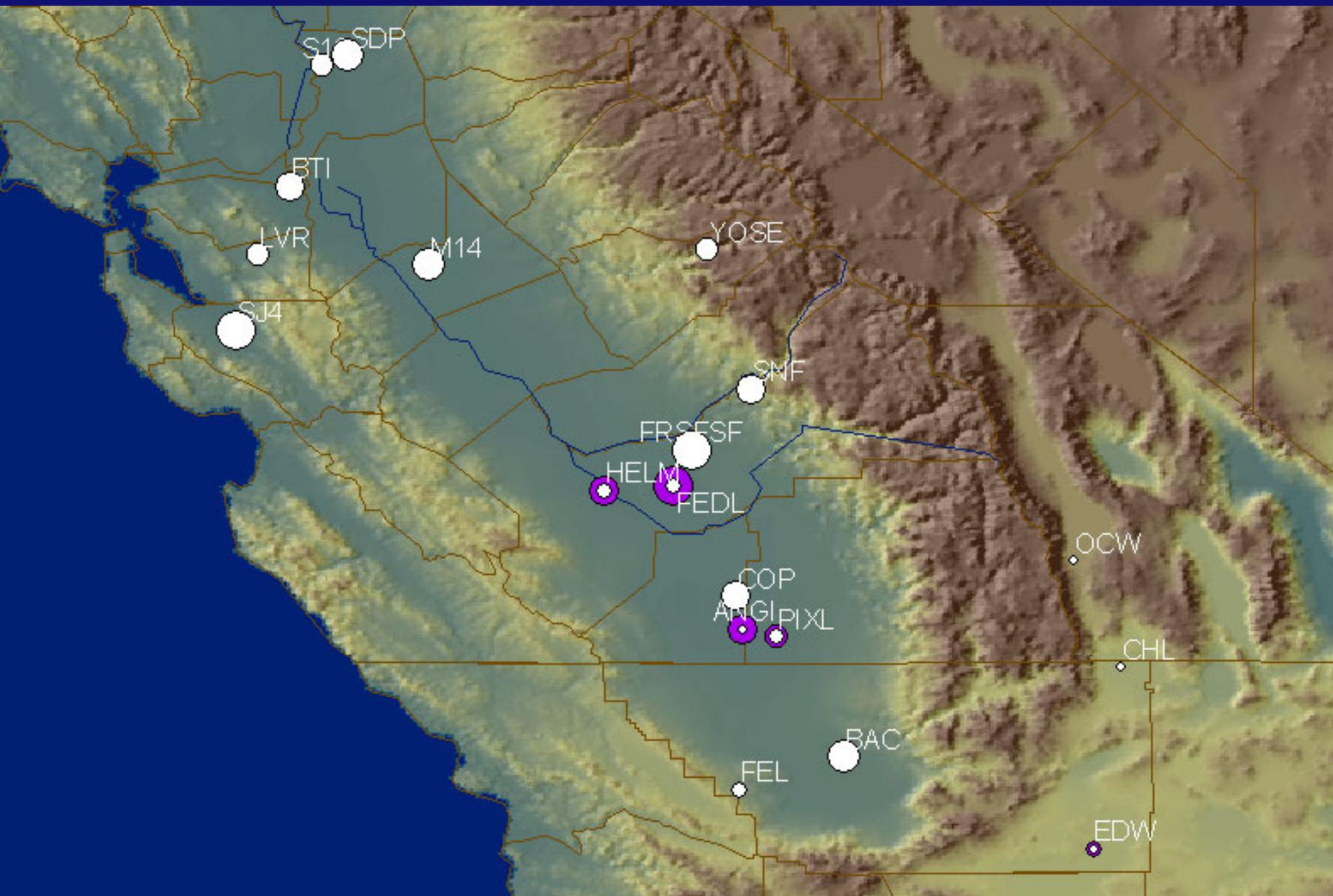
$$R^2 = 0.79$$



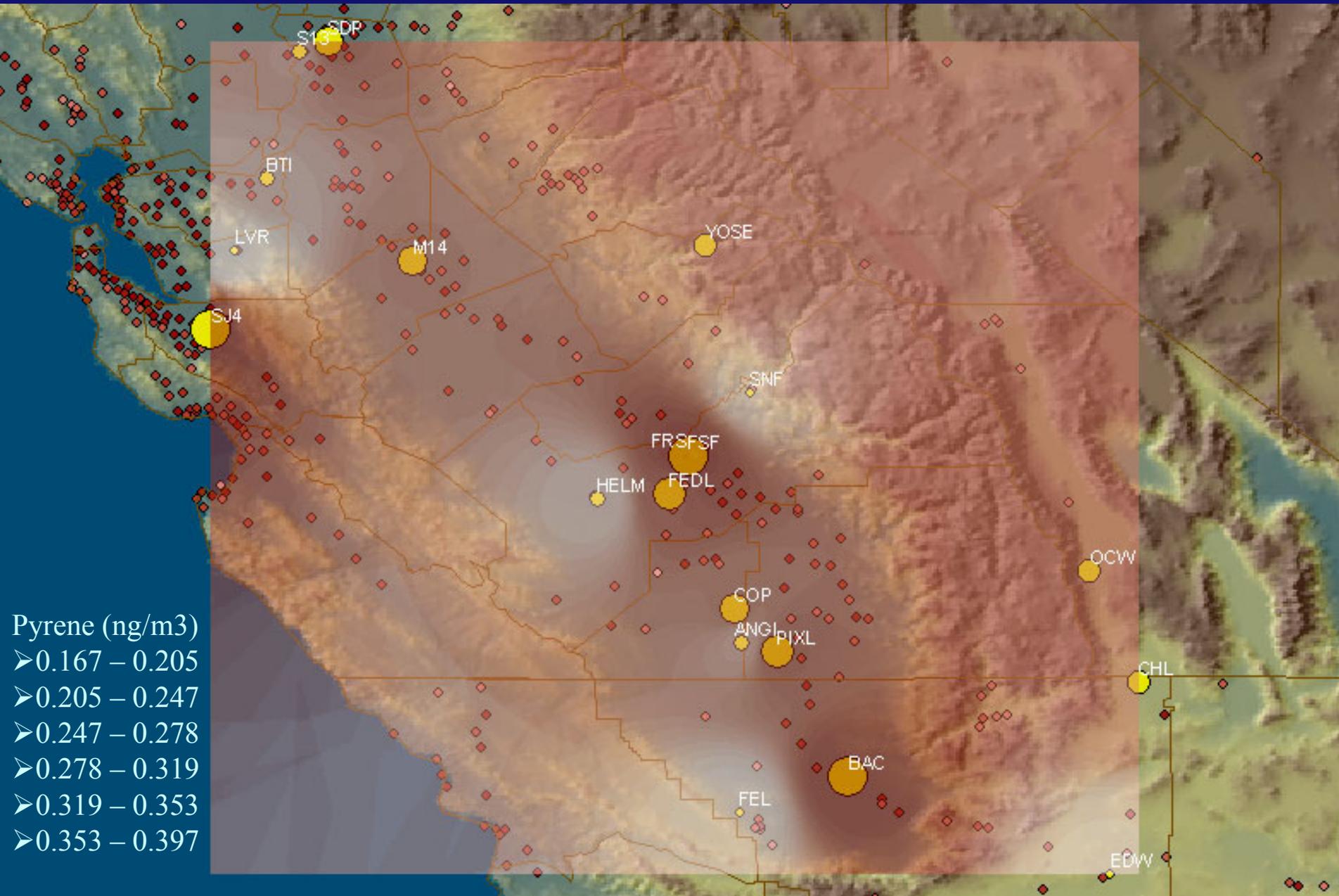
Adipic Acid (ng/m³)



Succinic Acid with Coronene Overlaid



IDW Prediction Map for Pyrene



Conclusion

- Individual organic species correlations between two Sacramento sites are quite good and between two Fresno sites are good
- Biomarkers for emission sources can be seen in the annual average characterization
- Spatial distribution for organic compounds differ between sites
- Site characterization is affected by local sources
- Assumptions about spatial distributions in between sites need to be made carefully and may not be accurate